Study on the alumina - silicon carbide - carbon based trough castable

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CERTIFICATE

*This is to certify that the thesis entitled, "**Study on the alumina - silicon carbide - carbon based trough castable**" submitted by Mr. **Venkatesh Pilli** (Roll No.: 613CR3003) for the degree of Master of Technology (Research) in Ceramic Engineering, National Institute of Technology, Rourkela, is a bonafide research work carried out by him under our supervision and guidance. His thesis, in our opinion, is worthy of consideration for the award of degree of Master of Technology (Research) in accordance with the regulation of the institute.*

The result embodied in this thesis is original and have not been submitted to any other university or institute for the award of any degree.

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Declaration

I hereby declare that my M.Tech (Research) thesis is entitled as **"Study on the alumina – silicon carbide - carbon based trough castable".** This thesis is my own work and has not been submitted in any form for another degree or diploma at any university or other institution of tertiary education. Information derived from the published and unpublished work of others has been acknowledged in the text and a list of references given in this thesis.

Venkatesh Pilli

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Abstract

Technological advancements in the iron and steel industries have changed significantly the operating practices of the blast furnace and to meet the challenges refractories are also getting changed and upgraded. Trough of blast furnace is important for transferring hot metal from blast furnace to transport vessel and the refractory lining of trough is subject to slag corrosion, oxidation, FeO corrosion from metal, abrasion and thermal / mechanical spalling etc. Trough refractories have changed from conventional hydrous clay-based material to anhydrous mass to SiC containing material, to Al_2O_3–SiC based low-cement castables. However, the presence of lime (cement) affects the high temperature properties and the performance of the refractory lining.

In the present work, Al_2O_3–SiC-C based trough castable has been studied with both cement and sol bonding. Different particle size distribution of the castable was also studied. The study compares the various refractory properties of Al_2O_3–SiC-C based trough castables, having different bonding system and flow behavior but with similar compositions. Also the effect of addition of spinel aggregates in the compositions with different bonding system was studied.

This comparative study showed improved dried strength for the cement containing compositions. Increasing amount of non-oxide components (like graphite or SiC) resulted in reduced densification and strength properties for both the bonding system at all the processing temperatures. Increasing amount of spinel in the composition was found to improve the corrosion resistance and sol bonding was found to provide better corrosion resistances than cement bonding against blast furnace slag.

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Chapter – 1
Introduction

1. Introduction:

Refractory is an inorganic, non-metallic material having those physical, mechanical properties that make them applicable to the structures or as components of a system that is exposed to environments above $1000^{o}F \approx 538^{o}C$ as per ASTM-C71.

Refractories are the materials which can withstand high temperatures, which are exposed to different mechanical stress and strain, thermal stress, and strain. They have high strength at room and higher temperatures, have corrosion, abrasion, wear, erosion and thermal shock resistance [1]. According to necessity of properties required based on application, different refractories are manufactured and designed. In some manufacturing units, more than one type of refractory is required according to the application area e.g. in steel-making, slag /metal are present at the same time at high temperatures. In the heat treating furnaces, oxidizing or solid/reducing gasses are present together.

1.1 Classification:

There are many ways to classify refractories; based on their: -

1. Chemical nature:
    - Acidic (Fireclay, silica, zircon, etc.).
    - Basic (Magnetite, Dolomite, Magnesia-carbon, magnesia-chrome etc.).
    - Neutral (Alumina, Carbon, Silicon Carbide, Mullite, Chromite etc.) [2],
2. Manufacturing method:
    - Shaped – Brick
    - Unshaped – Castable

There are other classifications also based on the constituents, purity, heat duty and insulating behavior. Monolithic or unshaped refractories are those which don't have the particular shape. They attain shape after application.

The majority of the refractories produced globally are used in the iron and steel industries [1]. The wealth of the refractory industries is very much dependent on the steel industries, almost 75% of the refractories produced globally are consumed in the steel industries. Steel consumption in India is expected to increase in coming years significantly as per proportion, finished steel consumption is far less than its regional counterparts. The development in the fields of infrastructure, construction, power and automobile sectors will continue to create significant demand for the steel, which in turn will create demand for refractories. Refractory business is a capital intensive industry which requires heavy investment in technology and basic raw materials [3].

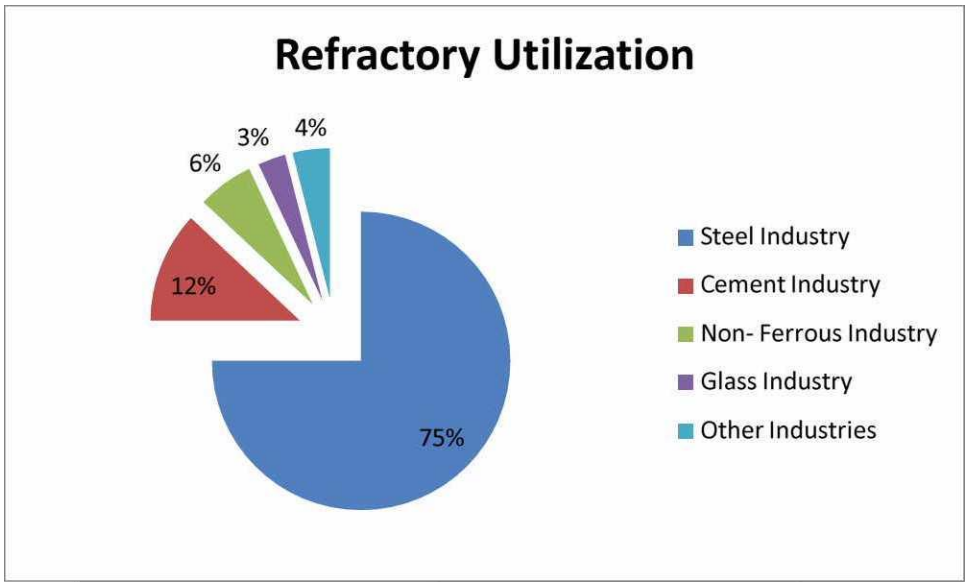

Figure 1.1 Consumption of refractory across various industry segments in India [4]

WORLD REFRACTORIES DEMAND (thousand metric tons)					
				% Annual Growth	
Item	2006	2011	2016	2006-2011	2011-2016
World Refractories Demand	35250	39150	46300	2.1	3.4
North America	3465	2695	2855	-4.9	1.2
Western Europe	3785	2960	3035	-4.8	0.5
Asia/Pacific	21470	27150	32900	4.8	3.9
Central & South America	1650	1675	2070	0.3	4.3
Eastern Europe	3090	2660	3015	-3.0	2.5
Africa/Mideast	1790	2010	2425	2.3	3.8

Figure 1.2 Global Refractories demand [5]

1.2 Advantages of Unshaped Refractories:

Nowadays, the demand and application of unshaped refractories have increased due to various advantages of it over conventionally shaped refractories like:

- Elimination of joints in the lining.
- Faster application.
- Ease of transportation and handling.
- Better scope to reduce downtime for repairs.
- Special skill for installation not required.
- Can be repaired easily without disturbing the whole structure, thus saving time, material and labor.
- Perfect choice for installing gas-tight walls and, hence, are more appropriate to construct pressure vessels operating at high temperatures and pressures.

Unshaped refractory linings are generally thinner than the corresponding brick structures. They are more durable, since building with bricks includes the use of mortars to join, thus creating weak points in the structure. The general categories of unshaped refractories are further classified on the basis of their application.

1.3 Classification of Unshaped Refractories:

1.3.1 Castable refractory:

More research is being carried in the area of castables when compared to other unshaped refractories. Castable consists of dry mixed aggregates which are mixed with water or other suitable bonding agent during the time of application. The material is generally applied by pouring or by pouring followed by vibration. Conventional castables are usually poured whereas low and ultra low cement castables are poured followed by a vibration.

1.3.2 Plastic refractory:

Plastic refractories are mixtures of refractory materials prepared in a stiff plastic condition for application without further preparation. As the name indicates, these refractories are made in a flexible form that could shape in any desired way. This form of refractory is ready to use and does not need to add any other ingredient on the site. They are generally rammed in place with a pneumatic hammer or pounded with a mallet, which is why they are sometimes called “ramming mixes.” Plastic refractories are easily adaptable for making quick, economical, emergency repairs and can be rammed to any shape or contour. According to the nature of bonding system, careful drying methods need to be followed to avoid unwanted deformities by rapid heating. Plastic refractories are supplied in a granular form for installation with special gunning equipment.

1.3.3 Ramming mass:

Ramming mixes essentially consist of ground refractory aggregates, with a semi-plastic bonding matrix which can be purchased in ready-to-use condition or prepared by adding water in the mixer at the construction site. Ramming mixes are filled behind a stable shuttering with the help of pneumatic hammers. They supply a denser, stronger refractory body than plastics, but initially they need some sort of support to restrain them when rammed.

1.3.4 Gunning mass:

Gunning mixes consist of graded refractory aggregate and a bonding compound, and may contain plasticizing agents to increase their stickiness when pneumatically placed onto a furnace wall. Gunning mixes are supplied dry, normally. They are installed by the use of a gunning equipment where the solid material is transported through hoses and then the liquid, usually water is added at the application nozzle. The success of the application depends on the skill of the installer since the water must be balanced and included at the nozzle depending on the flow of the dry material [6].

1.3.5 Spraying and Shotcrete mass:

Shotcrete is, in effect, a version of a cast-in-place concrete. Rather than placing concrete into forms, however, a fresh mix is sprayed onto wall panels that have been created in the shape of the structure. Shotcrete has been referred to by such terms as gunite. The preferred term today for all gunned material is Shotcrete. A nozzle man applies concrete from a pressurized hose to encompass the reinforcement and build up the wall thickness, forming structural shapes that include walls, floors, roofs, and other assemblies. The wide acceptance of Shotcrete is for slope/surface protection, tunnel lining, repairing existing structures, construction of swimming pools and special architectural shapes.

Compared to other unshaped refractories, castables have more demand in the areas of research, development and application [7]. Castable consists of graded dry refractory aggregates at the time of installation it is mixed with an appropriate bonding agent (typically water), usually cast or poured just as is done in case of normal concrete. However, in some cases they are vibrated, pumped, or shot pneumatically into place to form a shape or structure that becomes rigid due to chemical or hydraulic setting [1].

1.4 Bonding:

The majority of refractory castables use calcium aluminate cement as a binder (which is a hydraulic binder). It reacts with water at room temperature resulting in binding by the formation of coagulation – a crystallization network results from the formation of different calcium aluminate hydraulic phases [8].

Conventional cement bonded castables have limitations in high temperature applications due to the presence of higher lime content. Lime reacts with castable constituents, such as Al_2O_3, SiO_2 and basic components, forms low-melting phases [7, 9]. To evade the formation of low melting phases and to improve the hot strength properties the trend has been shifted to reduce the cement content and finally to use no cement in the castable. In recent years, other bonding systems have been employed. The decrease in lime content increases the hot properties of castable. Research has been confined for years to reduce the cement/lime content in the castable and to improve its hot strength properties. This has resulted in the continuing development of low and ultra-low-cement castables [7]. The most important changes to the castable refractories came since 1980s by the first commercial application of SiO_2-sol as a binder. SiO_2-sol is a colloidal form of SiO_2, follows the principle of sol–gel technology. Colloidal SiO_2 particles gel around the refractory

particles of the castable. Hence, a gel bonded castable is cement-less castable that develops initial strength through the gelation of the sol. A gel bonded castable forms the final fired matrix through the reaction between gel particles and reactive/finer components of the castable during firing. Because of no cement/lime, the chances of forming lime-based, low-melting phases are nullified, and this tremendously improves the hot properties of the castable [7].

Due to its high surface area, the gel is more reactive and can initiate the reactiion even at much lower temperature. In presence of reactive/finer alumina particles in the castable composition, silica sol particles react with them to form mullite at 1100–1150°C. In most refractories, mullite formation is important because of the excellent characteristics. Also, because of their higher viscosity, alkalinity and density, colloidal silica bonded castables are more cohesive and exhibit self-flowing characteristics [9]. In the case of cement bonded castables, silica fume is added to improve the flowability and some deflocculants and anti-setting agents also used.

1.5 Advantages of gel-bonded castables:

- Gel bond formulations do not require minor additives or deflocculants like the cement containing castables.
- Shorter drying time and so reduced drying flaws.
- Shows better refractoriness because of the absence of low melting phases like- anorthite or gehlenite.
- The gel is more viscous than water, helps to the maintain separation between refractory particles that, in turn, provide better resistance to thermal shock.
- Provides longer shelf life because there is no hydratable phase like LCC & ULCC.
- Longer campaign life, so less downtime and reduce the cost of furnace operation.

1.6 Blast furnace:

The blast furnace is a tall, vertical shaft furnace shown in fig 1.3, which employes carbon, mainly in the form of coke to reduce iron from its oxide ores. The raw materails of the blast furnace are iron ore (usually hematite Fe_2O_3, occasionally magnetite Fe_2O_4), coke and flux. The product is a liquid 'pig iron'(4-5% C, ½-1% Si) which is suitable for subsequent refining to steel [10]. The furnace gets its name from the method that is used to heat it. Preheated air at about 1000ºC is blasted into the furnace through nozzles near its base. The hot air blast to the furnace burns the coke and maintains the very high temperatures that are needed to reduce the ore to iron. Blast furnace is a high productivity unit which has, as its main purpose, rapid production of iron from the oxide ores [10, 11]. The reaction between air and the fuel generates carbon monoxide. This gas reduces the iron (III) oxide in the ore to iron.

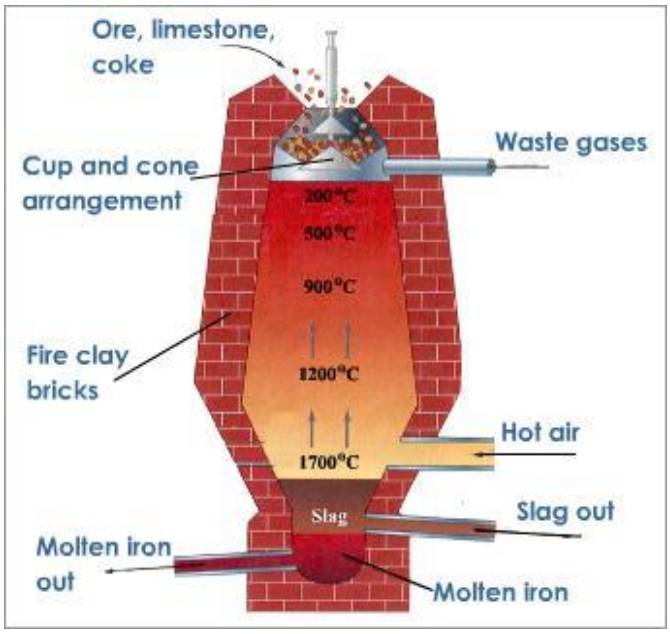

Figure 1.3 Blast furnace

$$Fe_2O_{3\,(s)} + 3CO_{(gas)} \rightarrow 2Fe_{(s)} + 3CO_{2\,(gas)} - - - \rightarrow Eq\ no.1$$

The final raw material in the iron making process is limestone. It is crushed and screened to a size that ranges from 0.5 inch to 1.5 inch to become blast furnace flux.

$$CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2\,(gas)} - - - \rightarrow Eq\ no.2$$

This oxide helps to remove some of the acidic impurities present in the ore. The impurities are removed and react with calcium oxide to make a liquid slag that floats on top of the molten iron.

$$CaO_{(s)} + SiO_{2\,(s)} \rightarrow CaSiO_{3\,(l)} - - - \rightarrow Eq\ no.3$$

The production of iron in a Blast furnace is a continuous process. The furnace is heated constantly and is recharged with raw materials from the top while it is being tapped from the bottom. Iron making in the furnace usually continues for about ten years before the furnace linings have to be renewed.

Long campaign life and large capacity have been the trend of the modern blast furnace. Higher blast and tapping temperatures, and higher utilization factor have forced much tougher working conditions on blast furnace troughs and runners. Principally because of higher temperature and larger flow, more stringent requirements in refractories are set not only in performance but also in installation [12].

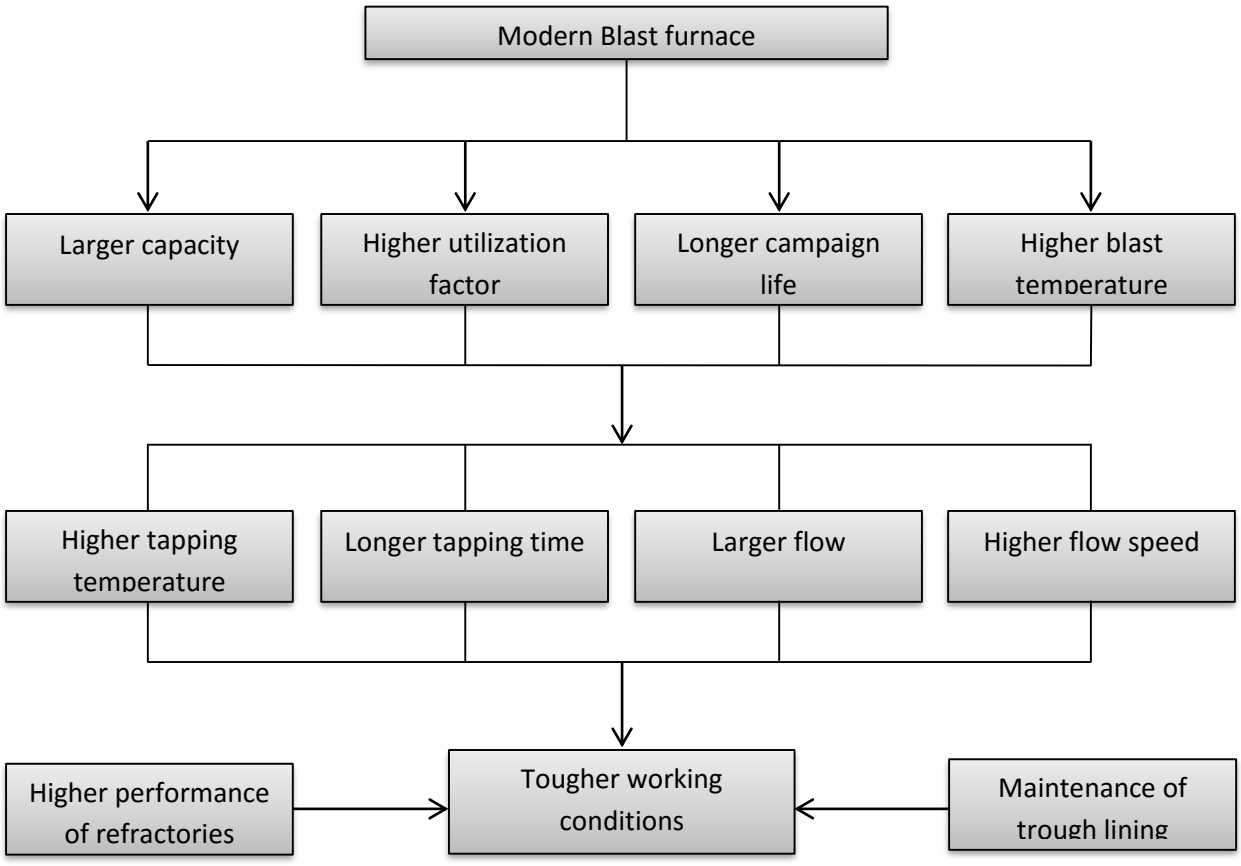

Figure 1.4 Requirements of modern Blast furnace

1.7 Trough of Blast furnace:

Cast house of Blast furnace consists of the main trough, iron runner, slag runner and skimmer block. The trough has prime importance in the cast house of the blast furnace because the slag and molten metal runs through it straight away after tapping. The trough refractory lining is subjected to slag oxidation and corrosion, FeO corrosion from metal, thermal/mechanical spalling and abrasion caused by molten metal and slag. Hence, the important requirements of the lining are corrosion resistance to slag and metal, non-wetting by metal and slag, high strength, oxidation resistance, high thermal shock resistance, and high abrasion resistance [12, 13]. The main trough is located in between tap-hole and skimmer block. Their gravity difference separates the slag, and molten iron. Slag passes through the upper region called as slag line, and the metal flows through the lower region called metal line. Castable of these two sections are designed for each operation conditions [13].

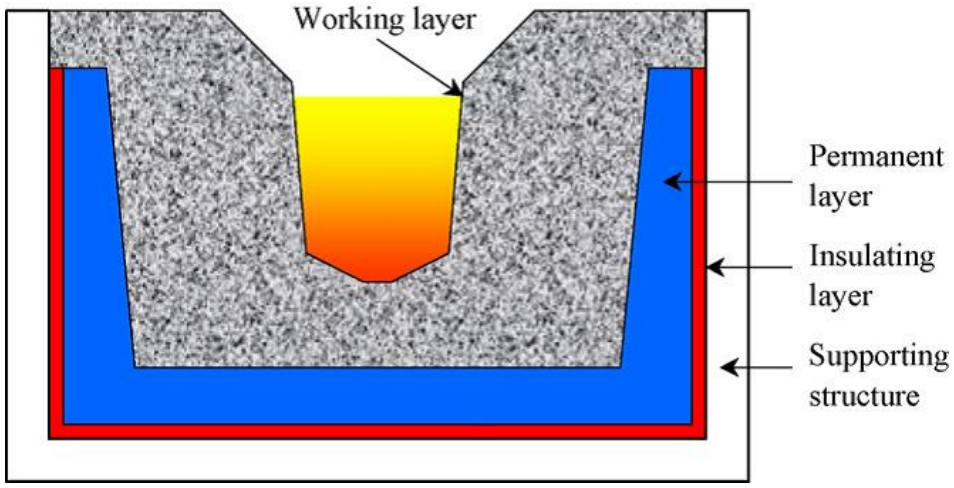

Figure 1.5 Blast furnace Trough

The main trough of the blast furnace contains several refractory layers enclosed in a metallic casing or structural concrete in few situations. Each layer has certain properties according to its

function. Working layer that comes first bears the most intense thermal loading consequent upon which it is frequently re-lined. Secondly, a permanent or safety layer, which is supposed to last 10-30 times longer than the first layer, supports less intense loads, and compensate any working lining damage. After these two layers, an insulating layer for protecting the structure from the excessive heat is given. The outer structure has either concrete or metallic casing [14].

Hence, the essential requirements of the lining are:

- Easy to install (suitable fluidity and hardening time)
- Corrosion resistance (resistance to slag and FeO attack)
- Abrasion resistance
- Oxidation resistance
- High strength
- Non-wetting by metal and slag
- Thermal spalling resistance

1.8 Trough castable:

Hydrous clay based material was used in the blast furnace trough, in the past, which provided short life. The trend has slowly shifted to use silicon carbide in the trough-lining for better thermal shock resistance and non-wetting features. Silicon carbide containing anhydrous ramming mass became the next application, which was then replaced by Al_2O_3–SiC-based low cement castables. Then carbon was incorporated in the refractory for better non-wetting and thermal-spalling properties [7, 12]. Al_2O_3 -SiC-C family of monolithic refractories are the most preferred one for the BFTs including main trough and slag/iron runner because of their high thermal conductivity, corrosion resistance, and thermal shock resistance [15, 16]. Alumina is the

major constituent in the BFT formulation. The higher the alumina content, higher the refractoriness of the mix. The presence of carbon increases the resistances against corrosion and thermal shock [17]. Silicon carbide has high thermal conductivity and resists well against erosion as well as slag attack and yields carbon, through oxidation, at elevated temperature [17, 18]. As a covalent chemical compound, silicon carbide inhibits sintering. Therefore, the strength like MOR, CCS, and HMOR decreases with increasing SiC content. Also, low wettability and the low reaction of silicon carbide significantly improve the slag resistance. Again, lower thermal expansion and higher thermal conductivity improve spalling resistance [19].

Carbon has many desired properties to use as a refractory material; however, the main drawback is its high susceptibility to oxidation [20]. Carbon is of utmost importance for corrosion resistance, high thermal shock resistance, and non-wetting nature. Carbon is added in various forms such as pitch, resin, coke, carbon black or graphite [21]. Metal additives, e. g. aluminum, silicon etc., which are added to the castable, act as anti-oxidants, which retard oxidation of carbon and also improve the hot strength by forming high-temperature ceramic bonds [15].

Properties needed for the trough castable are; hot strength, volume stability, corrosion, abrasion and thermal shock resistance. Both slag and metal are passed through the main trough, separated by their gravity difference. More SiC content is used in the slag line than metal line because the slag is more corrosive than the molten metal. Spinel material with lower silicon carbide content are used in the metal line for excellent resistance against FeO attack. Pre-formed and in situ spinel ($MgAl_2O_4$) containing refractory castables have been widely used as steel ladle linings, due to their high corrosion resistance to basic slag [22]. Magnesium aluminum spinel is incorporated in the Al_2O_3-SiC-C system because of its high corrosion resistance.

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Chapter – 2
Literature Review

2. Literature Review:

Refractory castables or concretes are the relatively new class of refractories. They have gained wide applications during the last decades. They have various advantages compared to conventional refractory bricks like application rate, cost, and flexibility, making them attractive to all other industrial users. Refractory castables consist of aggregates of coarse and fine refractory grains. They are bonded using a binder in the green state. Binder either transforms or volatilizes, during firing and assist in the formation of a ceramic bond. The most common binder used in castables is calcium aluminate cement (CAC) [1]. Castables are usually mixed with water at the time of application, then installed by either pouring or pumping. They acquire high mechanical strength at high temperatures and further improvements in properties occur after firing. They are resistant to high temperatures, mechanical stress, and thermal stress, chemical, and abrasive attack. They are primarily dependent upon the choice of refractory aggregate and hydraulic cement used; thus a wide variety of aggregates and several types of cement could be used to produce a lot of refractory concrete products with markedly different properties.

The quality of refractory concrete is improved through decreasing the cement content, i.e. 4–8% in low cement castables (LCC) or 1–3% in ultra-low cement castables (ULCC) or <1% in zero cement castables (ZCC). The LCC, ULCC, and ZCC have replaced many conventional castables, plastics, ramming and gunning mixes [2]. These concretes develop very high performance at heat and after heating. They are used extensively in refractory applications due to their excellent properties and ease of installation. They are used when thermal shock resistance or resistance against abrasion and corrosion by slags or melting metals is required [3].

2.1 Evolution of blast furnace trough castable:

With the progress of steel industry technology, large-scale blast furnaces with high efficiency and long lifetime were developed. The trough refractory lining is subjected to slag oxidation and corrosion, FeO corrosion from metal, thermal/mechanical spalling and abrasion caused by molten metal and slag [4]. Hence, the essential requirements of the lining are slag and FeO corrosion resistance, oxidation resistance, high thermal shock resistance, high strength, non-wetting by metal and slag, and high abrasion resistance [5].

In 1950s, refractories for blast furnace troughs and runners all over the world were the mixes of clay clinker and coke, with tar as the binder, lining by manual ramming. Great manpower and heavy labor were needed for frequently repairing and relining due to poor service performance. Later, anhydrous clay based ramming, clay-SiC compositions emerged and clay was replaced by alumina.

In 1960s and 1970s, as larger capacity blast furnaces were put into operation along with the development of new iron-making techniques, such as higher blast temperature and higher pressure operation, the blast furnace troughs and runners suffered from more severe working conditions. Al_2O_3-SiC-C ramming mixes were developed which showed better resistance to spalling and erosion by slag.

Since late 1970s, Al_2O_3-SiC-C castables for blast furnace trough have been developed and put into use, a large deal of work about monolithic refractories for blast furnace trough has been done all over the world and many new products and installation methods have also been developed [5]. Evolution of trough castable are shown in fig 2.1.

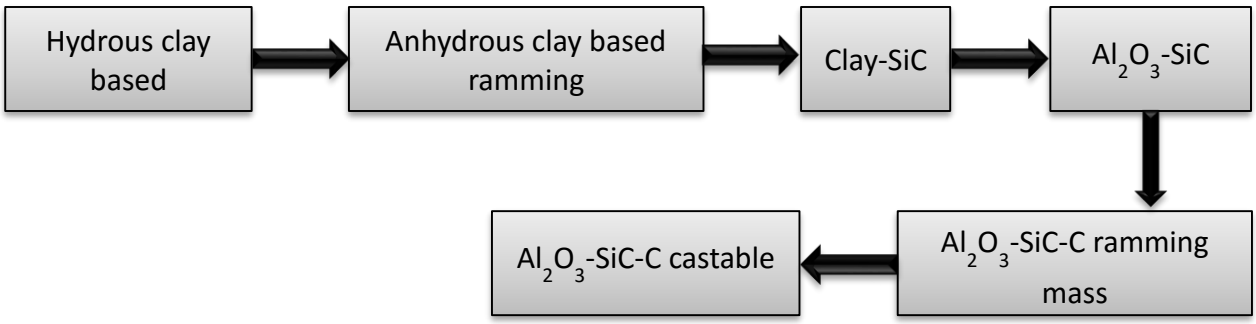

Figure 2.1 Evolution of trough castable

In the past, the hydrous clay-based material was used in the trough, which provided short life. The trend has slowly shifted to incorporate SiC in the trough-lining for better spalling and non-wetting characteristics. SiC, containing anhydrous ramming mass became the next application, which was then further replaced by Al_2O_3–SiC-based low cement castables. Then, carbon was incorporated in the refractory for better non-wetting and thermal-spalling properties [6].

2.2 Raw materials:

Al_2O_3-SiC-C family of monolithic refractories are the most preferred one for the blast furnace troughs including main trough / slag / iron runner because of its high corrosion and thermal shock resistance and thermal conductivity [7, 8]. These refractories are mainly fabricated using corundum, carborundum, micro α-Al_2O_3 powder, micro silica, and calcium aluminate cement as initial materials, which markedly improves the working life of the refractory materials used in blast furnace ironmaking systems. In addition, they provide the conditions required for large-scale production in blast furnaces [9]. These materials can improve the slag corrosion resistance of the refractories used in blast furnaces [10].

2.2.1 Alumina:

Alumina is the most commonly used oxide ceramic material. The majority of monolithic refractories dominated by high alumina or aluminosilicate materials. High-alumina refractory aggregates used in the formulation of monolithic refractories are composed of tabular alumina, white and brown fused alumina, calcined bauxite, calcined or sintered mullite and mullite-dominated alumina-silicates containing more than 50% alumina. High purity alumina materials are also used as calcined or highly reactive forms in the matrix for bonding phases. The characteristics and appropriate use of these need special attention in the formulation of monolithic refractories [11]. Alumina is the major constituent in the BFT formulation [6]. The higher the alumina content, higher the refractoriness of the mix [7]. Alumina is one of the most economical and broadly used materials for the family of engineering ceramics. High purity alumina is usable in oxidizing and reducing atmospheres up to 1925°C.

2.2.1.1 Tabular Alumina:

The tabular alumina is produced by the sintering of calcined alumina at approximately 1850°C. The end product contains large and plate-like crystals of alpha-calcined alumina, which gives it the name of tabular alumina. The fundamental principle for the production of tabular alumina is to produce a thermally stable and well-regulated microstructure.

Tabular alumina has the following typical characteristics:

- High chemical purity
- High solidity
- High melting point – 2,040°C
- Good resistance to thermal shock & Low shrinkage

2.2.1.2 Calcined Alumina:

Calcined alumina is an aluminum oxide that has been heated to temperatures in excess of 1050°C (1900° F) to remove chemically combined water. In this form, alumina has great chemical purity, high density, extreme hardness (9 on the Mohs hardness scale), and a high melting point (slightly above 2,050° C [3,700° F]). After calcination, the alumina particles appear as crystallite agglomerates, which are bigger when the degree of calcination is higher. The main characteristics of calcined aluminas are:

- The size of their crystallites vary considerably (between 0.5 and 10 μm).
- The morphology of its crystallites (rounded, angular,).

The major application areas of calcined aluminas include refractories, glass and enamel, tiles and porcelains, mechanical, electric and electronic ceramics, etc.

Benefits of Calcined alumina are:

- Enhanced refractoriness and performance
- Improved mechanical strength
- Abrasion resistance
- Thermal shock resistance
- Chemical inertness
- Dimensional stability
- High thermal conductivity
- Transparency

Due to the above mentioned beneficial properties, calcined aluminas are widely used in various applications.

2.2.1.3 Reactive Alumina:

"Reactive" alumina is the term which generally represents relatively high purity and small crystal size (<1 μm) alumina, which sinters to a fully dense body at lower temperatures than low soda, medium soda or ordinary-soda aluminas. These powders are supplied after intensive ball-milling which breaks up the agglomerates produced by calcination. They are utilized where exceptional strength, wear resistance, temperature resistance, surface finish or chemical inertness are required. Reactive Alumina powder is the fundamental constituent of high-quality refractory products like fine ceramics and castable refractories. Benefits of using reactive alumina are: -

- Reduced water demand
- Low open porosity
- Excellent sinter reactivity
- Excellent wear resistance and mechanical strength
- Excellent high-temperature mechanical performance for the final products
- Defined uniformed microstructure
- Very good corrosion resistance
- High dielectric strength
- Good thermal shock resistance
- Excellent high-temperature mechanical performance

2.2.2 Silicon Carbide:

Silicon carbide (SiC), also known as carborundum occurs in nature as the extremely rare mineral moissanite. SiC is produced in large tonnages, using the Acheson process by reacting a batch of high-purity sand and low-sulfur coke at 2200 - 2500^{o}C in an EAF.

$$SiO_2 + 3C \rightarrow SiC + 2CO_{(gas)} \quad ----\rightarrow Eq\ no.1$$ [12]

Commercial grades vary in the composition in the range of 90 - 99.5% SiC. Light green SiC is 99.8% pure, and as the purity decreases to 99%, the color changes to dark green and at 98.5% to black. >99.5% pure SiC are used for most abrasive and refractory applications. High-purity green SiC is used in high-performance ceramics and as resistance heating rods. In monolithic refractories, a wide range of purity of SiC is used depending on the application. The most common application of SiC is in the blast-furnace cast house where low-purity (90%) SiC is used. Higher purity SiC (97-98%) is used in ramming, gunning or plastics compositions used for thermal power stations since one of the main functions of the refractory is to conduct heat [11]. It is used in abrasives, refractories, ceramics, and numerous high-performance applications. Pure SiC are used for kiln furniture/ saggers.

Typical Silicon Carbide properties include:

- Good high-temperature strength
- High thermal conductivity and low thermal expansion
- Oxidation resistance (Reaction bonded)
- High hardness and wear resistance
- Excellent thermal shock resistance
- High corrosion resistance
- It may oxidize, but if oxidation is prevented it doesn't dissociate up to 2200^{o}C

2.2.3 Graphite:

Graphite is a crystalline form of carbon, a semimetal, and one of the allotropes of carbon along with the diamond. Graphite is the most stable form of carbon under standard conditions. Natural

graphite occurs in flake form, generally described as grayish black in color with a lustrous black sheen [2].

Due to its high-temperature stability and chemical inertness, graphite is a good material to use as a refractory. It is used in the fabrication of refractory bricks and the production of “Magnesia - carbon” refractory bricks (MgO-C). Graphite is also used to manufacture crucibles, ladles and molds for containing molten metals. Additionally, graphite is one of the most common materials used in the production of functional refractories for the continuous casting of steel.

The important uses of graphite are as follows:

- The major use of graphite is in the making of lead pencils of different hardness, by mixing it with different proportions of clay. The weakly held layers of carbon atoms in graphite easily slide over each other and are left behind on paper as black marks.
- Graphite is used as a dry lubricant in machine parts, due to its slippery nature,
- Being resistant to chemicals and having high melting point and also because it is a good conductor of heat, graphite is used to make crucibles.
- The presence of free electrons makes graphite a good conductor of electricity and it is used to make electrodes.
- Graphite can absorb fast-moving neutrons. Thus, it is used in nuclear reactors to control the nuclear fission reaction.

High-carbon-containing refractory castables are widely used in blast furnace troughs due to their high refractoriness, thermal shock resistance and low wettability by molten slag [13].

2.2.4 Calcium Aluminate Cement:

Calcium aluminate (CA) or high alumina cement remains to be the most important hydraulically setting cement used for bonding refractory castables (concrete) and gunning mixes [11]. Hydraulic bonding occurs with the help of the hydrates produced when the binder reacts with water at the room temperature. Calcium aluminate cement reacts with water resulting in binding by the formation of coagulation – a crystallization network which results in the formation of hexagonal tabular or acicular CAH_{10}, C_2AH_8, cubic granular C_3AH_6 crystals and alumina gel by means of the following hydraulic reactions:

$$CaO.Al_2O_3 + 10H_2O \xrightarrow{<21^oC} CaO.Al_2O_3.10H_2O - - - \rightarrow Eq\ no.2$$

$$2(CaO.Al_2O_3) + 11H_2O \xrightarrow{21-35^oC} 2CaO.Al_2O_3.8H_2O + Al_2O_3.3H_2O - - - \rightarrow Eq\ no.3$$

$$3(CaO.Al_2O_3) + 12H_2O \xrightarrow{>35^oC} 3CaO.Al_2O_3.6H_2O + 2(Al_2O_3.3H_2O) - - - \rightarrow Eq\ no.4$$

It takes some time for hydraulic binders to finish the hydraulic reaction. Therefore, the binders must be allowed some time for setting and hardening [1].

2.2.5 Colloidal Silica:

Colloidal silica is an aqueous colloidal dispersion of silica particles, which follows the principle of sol-gel technology. In sol-gel processing, colloidal particles or molecules in a suspension, a sol, are mixed with a liquid, which causes them to join into a continuous network, called a gel [12]. Colloidal silica being more viscous than the water helps to maintain more separation of refractory particles which, in turn, provide better thermal shock resistance [6]. Since the colloid grains are minute (10-20nm) and have a relatively large specific surface area, the grains

themselves are colorless and transparent, so they do not affect the natural color of the materials to be covered. When the moisture contained in silica sol is evaporated, the colloid grains firmly adhere to the material surface and the combination of silicon and oxygen are formed between grains. It is a good adhesive.

Colloidal silica is available in various particle sizes and concentrations. Usually, the larger sizes give more stable formulations and can be used in higher concentrations. The use of specific colloidal silica depends on the application. In general, 8 nm particles at 30% concentration and 15 nm particles at 40% concentration are used in refractory formulations [11].

2.2.6 Silica fume:

Silica fume, also known as micro silica, is an amorphous (non-crystalline) polymorph of silicon dioxide, silica. Silica fume is a by-product of ferrosilicon and silicon metal production. Silicon and Ferrosilicon are produced in large electrical smelting furnaces by the reduction of silica above 2000°C. The raw materials consist of quartz and carbon (such as coal, coke and wood chips). For ferrosilicon production, an iron source is also added.

The use of silica fume in refractory castables provides better particle packing. It allows for less water to be used while maintaining the same flow characteristics. It also promotes low-temperature sintering and the formation of mullite in the matrix of the castable.

2.2.7 Magnesium Aluminate Spinel:

Spinel is generally indicated by the formula AB_2O_4, where “A” is a divalent element such as Mg, Fe, Zn, Mn, Ni, Co, V, and Cu, and “B” a trivalent element such as Al, Fe, and Cr [14]. An enormous number of individual compounds and systems can justifiably be classified as spinels.

Among those spinels, $MgAl_2O_4$ and $MgCr_2O_4$ offer a good combination of physical and chemical properties such as high refractoriness, high mechanical strength, and high resistance to chemical attack, so they are consequently used to make a variety of spinel-containing refractories [15]. However the production of dense spinel product is a costly process. Magnesium aluminate spinel is eco-friendly and is widely used commercially and industrially due to the health and environmental hazards posed by the alternatives. Though $MgCr_2O_4$-containing refractories are still being used in many areas, due to the carcinogenic nature of Cr_6^+, they have been and are continuously being replaced by $MgAl_2O_4$-containing refractories [15, 2]. Spinel is mostly useful as refractory material and most commonly used in cement rotary kilns, glass tank furnaces, iron and steel industries.

Alumina-rich spinels are the largest volume of the refractory spinels; they are used as components of refractories for steel production. Their use is driven by two main sets of properties; thermal characteristics, such as improvements in the hot strength and thermal shock resistance; and resistance to corrosion by steel-making slag.

2.2.8 Anti-Oxidants:

The antioxidants (usually additives) play an important role in carbon-containing refractories to control the oxidation of carbon. The function of antioxidants is to avoid the oxidation. They melt or form low melting glassy phase and coats the carbon bonds to protect them from being oxidized. Anti-oxidants get oxidized and reduce the partial pressure of oxygen available to oxidize the carbon bonds.

However, the addition of antioxidants should be optimized to make a balance between the properties of oxidation and corrosion resistance. Metallic silicon, aluminum powder or

nonmetallic carbides such as Sic and B_4C were used as antioxidants (or additives) in the C refractories to improve the physical and thermo-mechanical properties. Aluminum (Al) is one of the most extensively used antioxidants in refractory compositions [13]. Aluminum reacts with graphite flakes to form compounds that affect the behavior of the refractory substances [16].

$$4Al_{(s)} + 3C_{(s)} \xrightarrow{Temp<932k} Al_4C_{3\,(s)} - - - \rightarrow Eq\ no.5$$

$$4Al_{(l)} + 3C_{(s)} \xrightarrow{Temp\geq 932k} Al_4C_{3\,(s)} - - - \rightarrow Eq\ no.6$$

The silicon reacts with the Carbon to form silicon carbide according to the following reaction [17].

$$Si_{(s)} + C_{(s)} \rightarrow SiC_{(s)} - - - \rightarrow Eq\ no.7$$

The formation of carbides increases the hot strength of the refractory.

2.3 Particle size distribution:

Slag penetrates into a refractory material via pores. Pores are usually characterized by pore parameters such as apparent porosity, permeability, pore size distribution and mean pore size. These parameters have close relationships with the refractory's slag resistance. For refractory castables, pores mainly result from two sources. One is related to the loss of water (either free water or bonded water in the cement hydration products) and/or organic components, and the other is related to the particle packing density which depends on the PSD indicated by the distribution modulus (q) value in the Andreasen's model. The PSD of a refractory castable has an important effect on its packing density and flowability [18].

Particle size distributions, as such, have been used for a number of years though, but on a rather limited scale; mainly for the coarser end of the distribution. New methods in PSD made it possible to analyze the sub-sieve fractions to a fuller extent. Achieving of 100% packing density

is not possible practically, control of the particle size distribution of a castable is important the particle size distribution dictates whether the castable is of a vibratable or a self-flowing type. Although a number of packing models have been presented over the last century, only a few have been used to any extent in the preparation of refractory castables [19].

2.3.1 Discrete approach to particle packing:

A discrete distribution consists of a small number of closely defined, discrete particles of various sizes. To create a dense pack, initially the coarse particles are to be packed, later the voids between the coarse particles are filled with medium sized particles, and finally the fine particles are used to fill the remaining gaps of the pack. The entire procedure is done without disturbing the pack at any stage.

But most powders are not monodispersions. A monodispersion is a system which contains all particles are of exactly the same size. Maximum powders are continuous distributions over wide ranges of sizes. The materials which are prepared chemically are not truly monodisperse because even when they are supposed to all be a single size, they will have some variations about their mean size. The discrete theory, however, is based on true monodispersions. Once it is packed, the discrete approach does not allow to move or stir the system. Stirring or randomly distributing distinct particle distributions is not possible according to the theory.

For making ceramics, coarse, medium, and fine particles are taken into a mixer for mixing; After mixing, other processes are used to form the ware. Such processes are not allowed by the discrete approach. Discreet approach gives a consistant packing only when the particles are packed one at a time, from coarse to fine. So the discrete approach is not a good approach to use to calculate the packing capability of a particle size distribution when the goal is to pack particles in the

course of making ceramic wares by all traditional methods. The method of packing described above is certainly not a traditional method [20].

2.3.2 Continuous approach to particle packing:

Most powders used for the fabrication of ceramics have a continuous distribution of particle sizes between some minimum and maximum size. For mixtures with discrete sizes, it was found that as long as the particles are very different in size, the packing density increased as the number of components in the mixture increases. Extending this concept to continuous distributions, a wide particle size distribution gave a higher packing density than a narrow particle size distribution [21].

Andreassen developed an approach to particle packing based on the use of continuous particle size distributions. In this approach, optimum packing occurs when the particle size distribution can be described by a power law equation commonly known as the Andreassen equation.

2.3.2.1 Andreassen's equation:

Andreassen's model of PSD is much simpler but has, to some extent undeservedly, been criticized because of its semi-empirical nature. One interesting factor of this model is that it does not require any shape factor. It only requires the different particles to be of similar shape [19, 22].

$$CPFT = \left(\frac{d}{D}\right)^{q} \times 100 - - - \rightarrow Eq\ no.8$$

Where,

CPFT = Cumulative percent finer than,

d = Particle size

D = Maximum particle size

q = Distribution modulus

For a refractory castable to achieve self-flow, the q value should be between 0.21 - 0.26 [18]. At lower q values the batch composition consists of high amount of fines, which aids to the better flow properties. Recent studies in this field revealed that a good flow can be achieved that q value not exceeding ~0.3. The castables having a q value near to 0.3 are vibratable type [18, 19].

2.3.2.2 Dinger and Funk equation:

The objections that have been raised against the Andreassen equation, that the model supposes infinitely small particles. To overcome this problem Dinger and Funk made a modified Andreassen equation in which, minimum particle size incorporated [19, 20].

$$CPFT = \left[\left(D^q - D_s^q\right)/\left(D_l^q - D_s^q\right)\right] \times 100 - - - \rightarrow Eq\ no.9$$

Where,

CPFT = Cumulative percent finer than,

D = Particle size

D_s = Minimum particle size

D_l = Maximum particle size

q = Distribution modulus

The exponent q is same for both models. Continuous particle size distributions can be mixed to improve the packing density. The error in Andreassen's approach is that he did not recognize a smallest particle size, D_s. Straight lines on log-log plots continue forever. They can reach huge numbers on the one extreme, and they can reach especially small values at the other extreme.

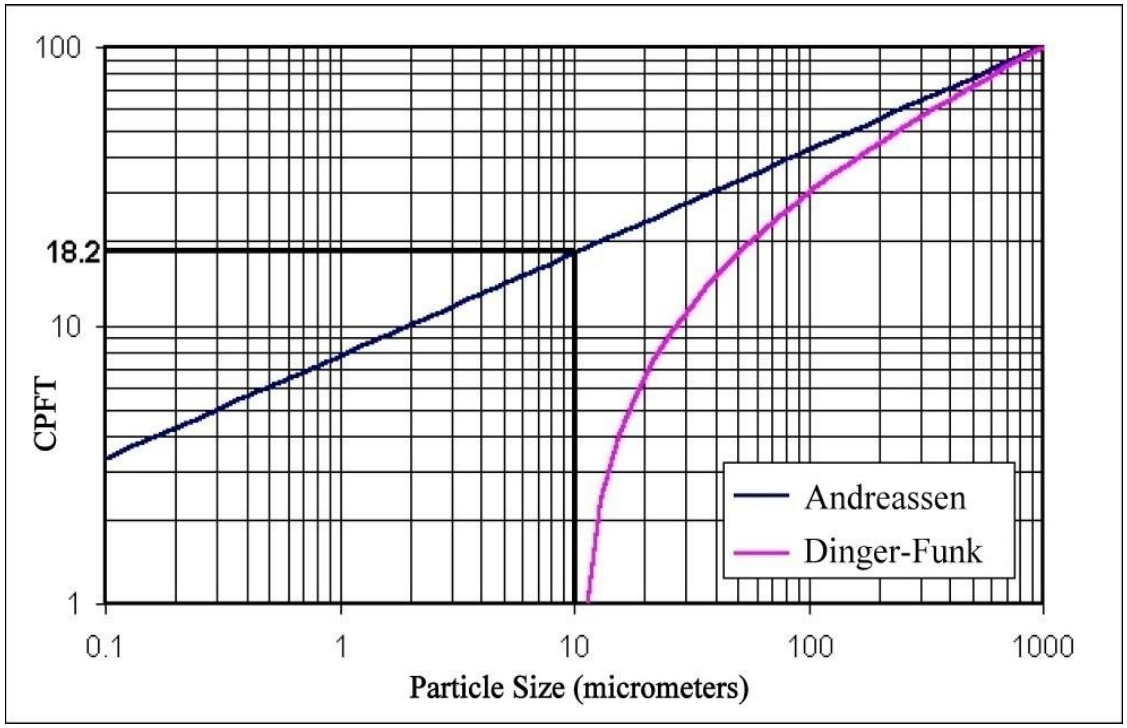

Figure 2.2 Andreassen and Dinger-Funk particle size distributions with q=0.37 [20]

Figure 2.2 shows an Andreassen distribution with a largest particle size, D_L = 1000 micrometers and a distribution modulus, n = 0.37, and a Dinger-Funk distribution with a D_L = 1000 micrometers, a D_S = 10 micrometers, and a distribution modulus of q= 0.37.

It may be noted that the Andreassen distribution in fig 2.2 continues off towards smaller and smaller sizes at the left edge of the diagram. Two decades off the chart to the left is 1 nanometer (10 Angstroms). It is not possible to have a particle of a particular crystal that much small. Any particle of any distinct mineral will be larger than that [19, 20, & 22].

2.4 Effect of Spinel content on Refractory castables:

Magnesium aluminate spinel offers a unique combination of high-temperature properties including a high melting point, excellent resistance against chemical attack, potentially high strength even at high temperatures and very good thermal characteristics [15, 23]. Pre-formed and in situ spinel ($MgAl_2O_4$) containing refractory castables widely used for industrial applications, particularly in steel ladle linings, due to their outstanding thermo-mechanical properties, extended service life and high corrosion resistance to basic slag [24, 25 & 26]. Fine spinel formed "in situ" by the reaction of MgO-Al_2O_3 in the matrix of alumina-magnesia castables increases resistance to corrosion and slag penetration compared to alumina-spinel(spinel-containing) castables [27, 28 & 23].

In situ spinel formation in the castable matrix, by adding magnesia to the high-alumina composition, could result in finer spinel and a better distribution throughout the refractory microstructure, increasing slag penetration and corrosion resistance [24]. Pre-formed spinel castables present high volumetric stability and do not have the problems like MgO hydration and expansive behavior at high temperatures like in situ spinel. Preformed spinel is added to alumina castables for two major purposes: to increase the slag resistance and to improve the thermo-mechanical properties [29].

Pre-formed or in situ spinel containing castables present different formulation concepts: whereas alumina–magnesia compositions require silica fume in their composition, mainly in order to counterbalance the in situ spinel expansion effects, preformed spinel castables can be produced without adding silica fume [24]. Different ways of spinel incorporation result in particular properties to the refractory material, a castable containing both in-situ and pre-formed spinel

might present balanced properties and suitable performance in steel ladle applications [30]. Whereas too little spinel content leads to a high corrosion rate, a too high one results in high penetration. Besides, the total amount of spinel, its particle size, also affects the corrosion resistance and the finer the spinel grains, the higher is the corrosion resistance [24, 28].

These properties make magnesium aluminate a superior class of refractory material. But the requirement of highly pure raw materials and the processing costs are expensive for commercial success. A commercially acceptable solid state reaction synthesis process from oxide reactants is associated with a counter diffusion process of Mg^{2+} and Al^{3+} ions in a rigid oxygen lattice. This process has a volume expansion of about 5 %, which has a negative effect on the sintering process, so a two-stage firing is required to obtain sintered spinel aggregates, which affects the cost of the product. Magnesium aluminate spinel has always had an environmentally friendly advantage, so it has received favor from researchers, scientists and industrialists all over the world [15].

2.4.1 Effect of Calcium Aluminate Cement:

The corrosion rate increases with the increase in the amount of cement content in the composition, but penetration decreases. The formation of calcium aluminate phases (CA, CA_2, and CA_6) results in a highly densified layer with low open porosity (<10%). When associated with the alumian and the presence of spinel, CAC-bonded castables can attain an optimized basic slag resistance. Al_2O_3 - MgO refractory castables containing hydratable alumina as the dominant binder, exhibit better slag infiltration resistance and lower erosion compared to CAC composition. The chemical attack of the bond system took place firstly in the CaO–MnO–FeO-rich liquid slag and the matrix components (calcium aluminates and alumina). Thus, the local

liquid (predominantly $CaO–Al_2O_3–SiO_2$) presented a higher amount of CaO that could react with the grain (leading to CA_6 formation). After the dissolution of the finest particles of the matrix, the resultant liquid would prone to attack the grains [24].

2.5 Al_2O_3-SiC-C based Trough castable:

Trough castables are exposed to different wear mechanisms during operation, the propagation of metal/ slag into it cause corrosion and erosion to the refractory castable. Some of these wear mechanisms include thermal shock, iron erosion, and slag corrosion. Sudden and rapid changes in temperature, which relates to thermal shock, may cause the stresses to develop within the refractory castable, affect the life of the lining. These stresses reduce the service life through the generation of cracks. Molten iron may also attack the castable constituents such as silica and other oxides and deteriorate the properties of the refractory material [31]. Slag attacks the trough castable by forming low-melting phases through several chemical reactions which makes the castable more susceptible to wear. Generally, trough castables are designed to resist these different wear mechanisms through the use of particular types of raw materials in the formulation of the trough castable. Trough castables are typically comprised of alumina-silicon carbide-carbon (Al_2O_3-SiC-C).

The $Al_2O_3–SiC–C$ refractories are mainly fabricated using corundum, carborundum, micro α-Al_2O_3 powder, micro silica powder, and calcium aluminate cement as starting materials, which significantly improves the working life of the refractory materials used in blast furnace ironmaking systems. In addition, they provide the refractory conditions essential for large-scale production in blast furnaces. However, corrosion caused by liquid oxides is one of the most severe modes of degradation that limits the lifetime of the refractory linings. Alumina is the

primary constituent in blast furnace trough castables [7]. The high alumina aggregate has high density and low porosity to provide good resistance to metal and slag attack [31]. Carbon is added as a non-wetting compound to avoid adhesion of iron and slag to the castable [32]. Consequently, carbon-containing and carborundum-containing refractory castables are widely used in blast furnaces due to their high refractoriness, thermal shock resistance, and low molten slag wettability. Silicon carbide acts as a volume stabilizer to minimize linear change when in service and increases the thermal conductivity of the refractory material [33, 31]. The volume stability and higher conductivity characteristics of the silicon carbide help minimize damage from thermal shock. Fine aluminas and silicas are also typically added to trough castables to help promote good flow properties. Metals, such as silicon or aluminum, may also be added as antioxidants to protect the carbon, to aid in dry-out and to enhance the hot strength of the refractory material [7, 31]. Incorporation of these raw materials into the refractory composition is expected to increase the complexity of the matrix particles, this was mainly caused by the non-oxide nature of silicon carbide and the decreased wetting ability of carbon [9]. These materials can improve the slag corrosion resistance of the refractories used in blast furnaces [10].

2.5.1 Effect of Cement content:

The trend in castables has been to decrease cement content and finally to use no cement in the castable for high- or self-flow-ability. Due to the presence of lime, cement bonded castable has limits in high-temperature applications. Lime forms low-melting phases on reaction with castable constituents, such as Al_2O_3, SiO_2, and basic components which resulted in poor high-temperature properties. Research has been confined for decades to decrease the cement/lime content in the castable and to improve its hot strength properties. This has resulted in the continuing development of low cement and ultra-low-cement castables [6]. Due to reduced cement content

and higher packing density, the water demand in high-alumina castables is decreased remarkably. Therefore, both LCC and ULCC exhibit better physical properties than the traditional medium-cement castables [9].

At present, low and ultra low cement castables are based on alumina-containing mineral fillers and SiC have gained wide acceptance as materials for hot metal and slag runners. Silicon carbide is introduced for enhancing the erosion and corrosion resistance of the composite under operating conditions [34].

2.5.2 Effect of Silica Sol:

SiO_2-sol as a binder has brought about the most significant changes in castable refractories. SiO_2-sol is the colloidal form of silica; colloidal SiO_2 particles gel around the refractory particles of the castable. Colloidal silica particles can be linked together using different setting mechanisms, such as gelling and coagulation, providing initial strength when applied to ceramic systems. Concerning gelling, the interaction of silica particles triggers the siloxane bonding (Si–O–Si) and the build-up of a three-dimensional network [35]. Hence, a gel-bonded castable is basically a cementless castable that develops initial strength through gelation of the sol, thus the absence of RO group (such as CaO, MgO or FeO) allows a better ceramic bond in the castable without formation of low-melting phases [36].

A gel bonded castable forms the final fired matrix through reaction between gel particles and reactive/finer components of the castable while firing [6]. Because of its high surface area, the gel is highly reactive and can initiate the reaction at a much lower temperature. In the presence of reactive/finer alumina particles in the castable composition, silica sol particles react with the

alumina particles to form mullite at 1100–1150°C [36]. Mullite provides a high-temperature ceramic bond and hot strength in the products, and it imparts better thermal-shock resistance [6].

2.5.3 Effect of Silicon Carbide:

Silicon carbide is introduced into the trough castable to enhance the thermo-mechanical properties of the composite under operating conditions [34]. Slag resistance of the castable significantly increases with the increase in the amount of Silicon carbide due to the low wettability and low reaction of Silicon carbide. In Al_2O_3–SiC–C based mix, the Al_2O_3 reacts with blast furnace slag and results in erosion. However, the slag has little erosion on SiC and C. Silicon carbide possesses the advantage of inhibiting sintering shrinkage and increases the thermal conductivity of the refractory material [31]. For Iron line, the temperature varies in a small range during service condition, for which no spalling damage occurs. The main erosion is caused by the reaction of silicon carbide oxidation.

$$SiC + 2FeO \rightarrow SiO_2 + 2Fe + C \longrightarrow Eq\ no.10$$

Slag erosion is minor. Slag resistance of the castable increases with increase in amount of silicon carbide. Increase in non-oxide components in the batch reduces the chances of direct bonding among alumina particles, thereby reducing the sintering and densification, consequent upon which strength will decrease. Instead of using one kind of mix for the trough, it is always better to use two kinds of the mix - low SiC containing castable for the iron line, and high SiC containing castable in the slag line [33].

2.5.4 Effect of Spinel:

The main trough is usually designed with a zone lining, which implies that the composition of the refractories in the slag line and metal line could be distinct. Al_2O_3–SiC–C castables usually

contain a high amount of SiC (15–20 wt%) in order to improve their corrosion and thermal shock resistance. However, the high oxidation of SiC by FeO is the main cause of refractory wearing when they are applied to the metal zone. Thus, one alternative to reduce this effect consists of adding MgO or $MgAl_2O_4$ as a component of trough castables, which could provide a higher FeO corrosion resistance [37]. On the other hand, spinel accelerates the oxidation of SiC. SiC is effective to reduce slag penetration and spinel is effective to improve slag corrosion resistance [38].

2.5.5 Effect of Spinel on oxidation of SiC:

Spinel increases the corrosion resistance of the castable, instead of that spinel influences the oxidation of SiC. SiC is oxidized under co-existence with solid carbon, the oxidation mechanism described by the following reactions:

1. Active SiC Oxidation under reducing atmosphere:

$$C_{(s)} + \frac{1}{2}O_{2\,(g)} \rightarrow CO_{(g)} \quad Eq\ no.\ 11$$

$$SiC_{(s)} + CO_{(g)} \rightarrow SiO_{(g)} + 2C_{(g)} \quad Eq\ no.\ 12$$

$$SiO_{(g)} + CO_{(g)} \rightarrow SiO_{2\,(s)} + C_{(s)} \quad Eq\ no.\ 13$$

2. $Mg_{(g)}$ release from the spinel grains in a reducing atmosphere.

$$MgO.Al_2O_{3\,(s)} \rightarrow Mg_{(g)} + \frac{1}{2}O_{2\,(g)} + Al_2O_{3\,(s)} \quad Eq\ no.\ 14$$

3. Acceleration of SiC oxidation:
    - The oxygen released (Eq. (14)) will induce $CO_{(g)}$ generation and, consequently, SiC oxidation.

- $SiO_{(g)}$ can also react with oxygen and increase the $SiO2_{(l)}$ amount.

$$SiO_{(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow SiO_{2\,(l)} - - - \rightarrow Eq\ no.15$$

The partial pressure of $SiO_{(g)}$ from SiC and $Mg_{(g)}$ from spinel (presented in the reacting environment) could affect the oxidation rate of the trough castable. $Mg_{(g)}$ produces the liquid phase in pore by the reaction with the matrix of the material. This liquid has a solubility of SiO_2, so $SiO_{(g)}$ in the material dissolves into the liquid. The consumption of $SiO_{(g)}$ lowers its partial pressure. $SiO_{(g)}$ which should keep equilibrium pressure would be provided by silicon carbide. Thus, spinel accelerates the oxidation of silicon carbide [37, 38].

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Objective of the Work:

- Preparation of Al_2O_3-SiC-C trough castable with different bonding (cement & sol) systems with different particle size distributions (q=0.21 & 0.29).
- Preparation of castables with both cement and sol bonding with varying in amounts of SiC and C content.
- Evaluation of variation in properties for both bonding systems with the variation of C and SiC content.
- Evaluation of corrosion resistance and other properties with incorporation of spinel with both cement and sol bonding systems.

Objective of the work is a comparative study between sol & cement bonding in Al_2O_3-SiC-C based trough castable with varying amounts of C and SiC and with the addition of Spinel.

Chapter – 3

Experimental Work

3. Experimental Work

3.1 Raw materials:

Tabular Alumina

Alumina Fines

Silicon Carbide

Spinel

Graphite

High Alumina Cement

Fume Silica

Silica Sol

Figure 3.1 Starting Raw materials

Table 3.1 Details of the starting Raw materials

Constituent	WTA Grain Almatis	Alumina Fines Almatis	Fume Silica Elkem	HAC Almatis	SiC Saint-Gobain	Silica Sol Dr. Khan's	Spinel Almatis
SiO_2	0.03	0.03	96.2	0.21	0.35	29.8	0.10
Al_2O_3	99.34	99.3	0.4	71.64	0.22		≥74
Fe_2O_3	0.035	0.03	0.1	0.11	0.1		0.15
TiO_2		Trace					
CaO		0.02	0.2	26.91			0.24
MgO		0.01	0.1	0.32			22.5
Na_2O+K_2O	0.15	0.1	0.4	0.27			0.09
SiC					98.1		
LOI						70.1	

Property	WTA Grain	Alumina Fines	Fume Silica	HAC	Silica Sol	Spinel
Particle size, µ		D_{50} = 2.5	>99% <45		~ 0.02	1-0.5mm
Bulk density	3.61 gm/cc					3.3 gm/cc
Apparent porosity	3.93%					1.8%
Sp. Surface area		3.1 m^2/gm	20 m^2/gm	0.44 m^2/gm		
Phase analysis	Corundum	Corundum	Amorphous	CA_2, CA		Spinel

CA= Calcium aluminate and CA_2 = Calcium di aluminate

The starting raw materials were white tabular alumina (WTA) of different fractions, alumina fines (RA), silicon carbide (SiC), graphite (C), magnesium aluminate spinel, Al metal powder as anti-oxidant and calcium aluminate cement or silica sol as binder. The details of the raw materials are given in table 1, shown in fig 3.1. Castable formulation was done using the particle size distribution (PSD), as proposed by Dinger and Funk [11],

$$CPFT = \left[\frac{(D^q - D_s^q)}{(D_l^q - D_s^q)}\right] \times 100 \text{ --- Eq. 1}$$

Where,

CPFT: Cumulative percent finer than,

D: particle size, D_s: minimum particle size,

D_l: maximum particle size,

q: distribution modulus.

Castables with both cement bonded and sol bonded prepared

- with varying in amounts of SiC, C, with different particle size distributions (q = 0.21 & 0.29)
- with varying in amounts of C and Spinel

3.2 Particle size Distribution:

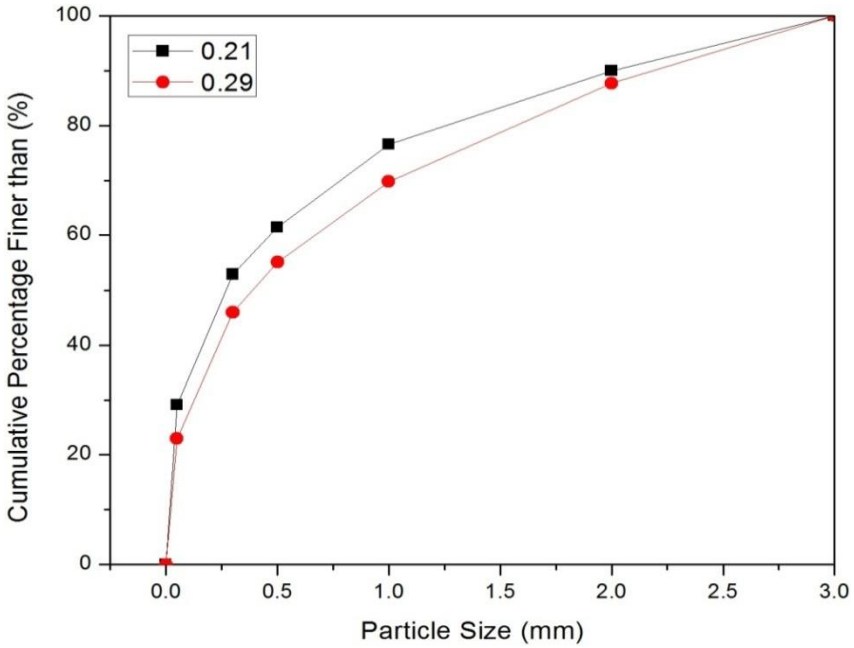

Figure 3.2 Particle size distribution used in this work

3.3 Batch compositions without Spinel:

Table 3.2 Sol bonded compositions with q = 0.21

Material	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6
WTA	60.87	55.87	50.87	60.87	55.87	50.87
RA	26.13	26.13	26.13	24.13	24.13	24.13
SiC	10	15	20	10	15	20
C	2	2	2	4	4	4
Al powder	1	1	1	1	1	1
SiO_2 sol	6.7	6.5	6	6.25	6.25	6.25

Table 3.3 Cement bonded compositions with q = 0.21

Material	Batch 1	Batch 2	Batch 3	Batch 4	Batch 5	Batch 6
WTA	60.87	55.87	50.87	60.87	55.87	50.87
RA	17.73	17.73	17.73	15.73	15.73	15.73
SiC	10	15	20	10	15	20
C	2	2	2	4	4	4
Cement	4	4	4	4	4	4
Fume silica	4	4	4	4	4	4
Al powder	1	1	1	1	1	1
Darvan C	0.3	0.3	0.3	0.3	0.3	0.3
Citric acid	0.1	0.1	0.1	0.1	0.1	0.1
Water	6.07	6.08	6.08	6.12	6.25	6.25

Table 3.4 Batches of both cement and sol bonding compositions with q = 0.29

Material	Sol-bonded		Cement-bonded	
	Batch 1	**Batch 2**	**Batch 1**	**Batch 2**
WTA	62.06	62.06	62.06	62.06
RA	19.94	17.94	11.54	9.54
SiC	15	15	15	15
C	2	4	2	4
Cement	-	-	4	4
Fume Silica	-	-	4	4
Al powder	1	1	1	1
Darvan C	-	-	0.3	0.3
Citric acid	-	-	0.1	0.1
SiO_2 sol / Water	6	6.25	6	6.25

3.4 Batch compositions with Spinel:

Table 3.5 Sol bonded compositions with q = 0.21

Material	Batch 1	Batch 2	Batch 3	Batch 4
WTA	50.87	45.87	50.87	45.87
RA	26.13	26.13	24.13	24.13
SiC	15	15	15	15
C	2	2	4	4
Spinel	5	10	5	10
Al powder	1	1	1	1
SiO_2 sol	6.25	6.25	6	6.12

Table 3.6 Cement bonded compositions with q = 0.21

Material	Batch 1	Batch 2	Batch 3	Batch 4
WTA	50.87	45.87	50.87	45.87
RA	17.73	17.73	15.73	15.73
SiC	15	15	15	15
C	2	2	4	4
Spinel	5	10	5	10
Cement	4	4	4	4
Fume silica	4	4	4	4
Al powder	1	1	1	1
Darvan C	0.3	0.3	0.3	0.3
Citric acid	0.1	0.1	0.1	0.1
Water	6.5	6.25	6	6.12

3.5 Sample Preparation Process

3.5.1 Mixing:

The purpose of mixing raw materials with binder is to achieve homogeneous mixture that can be successively molded or shaped by using fabrication methods. All the raw materials were first dry mixed as per batch compositions (Table 2-6) in a Hobart mixer. SiO_2-sol or water was added to the dry mixed batches during mixing in sol or cement-bonded castable compositions at an amount of 6-7 volume to weight percent. Mixing was continued thoroughly till proper consistency / flowability was achieved.

3.5.1.1 Hobart Mixer:

Hobart mixer is a planetary mixer shown in fig 3.3. The planetary mixer is named for its complete three dimensional mixing methods. The blades in a planetary mixer each rotate on their own axis, and at the same time on a common axis, thereby providing complete mixing in a very short time. As a general rule, planetary mixers offer a greater degree of mixing compared to spiral or generic mixers.

Figure 3.3 Hobart mixer

3.5.2 Casting:

Casting is a manufacturing process by which a liquid material is usually poured into a mold, which contains a hollow cavity of the desired shape, and then allowed to solidify.

Mixed batches, then were cast into 50 mm cube-shaped lubricated molds (fig 3.5) on a vibratory table (fig 3.4) which vibrates at 3200-3600 vibrations/min with amplitude of $\pm$0.5 mm.

Figure 3.4 Table vibrator

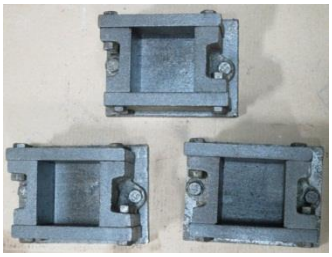

Figure 3.5 50mm cube shaped molds

3.5.3 Aging:

Cast products were then cured in humid condition within the mold for 24 h, and then demolded. Humid condition for maintaining the same atmosphere, otherwise due to the difference in drying for surface and the body cracks will generate.

3.5.4 Drying:

The demolded products were air dried for 24 h and further oven dried at 110°C for 24 hr in a hot air oven (hot air is circulating inside) for removing the physical water present in the system.

3.5.5 Firing:

Dried products were fired at 900 & 1500°C with 1 h soaking time in chamber furnace (fig 3.6), in atmospheric condition. At 900°C the de hydroxylation takes place, after 1150°C formation of ceramic bond starts.

Figure 3.6 1700°C Chamber furnace

The bulk density (BD) and cold crushing strength (CCS) of the dried, 900^{o}C and 1500^{o}C heat treated samples were measured. 1500^{o}C fired composites were also characterized for corrosion resistance, phase analysis and microstructural analysis.

3.6 Characterizations of composite:

3.6.1 Bulk density:

Bulk density of the dried (110°C) and fired (900 & 1500°C) samples were measured. Sample weight measured by weighing balance. Dimensions measured by using a digital Vernier Caliper.

$$Bulk\ density\ (BD) = \frac{mass\ (gm)}{volume\ (cc)}$$

The density values were calculated in gm/cc.

Figure 3.7 Measurement of dimensions

3.6.2 Cold crushing strength:

The cold crushing strength (CCS), the maximum load per unit area, applied at a specified rate that a material will withstand before it fails at room temperature.

Cold crushing strength of the dried (110°C) and fired (900 & 1500°C) samples were measured. CCS was measured by placing the sample in pressing machine (fig 3.8); the load is applied on the surface of sample at a constant rate. The load at which the sample breaks represents the cold crushing strength.

Figure 3.8 Pressing machine

$$Cold\ crushing\ strength\ (CCS) = \frac{load\ (KN)}{area\ (cm^2)}$$

The cold crushing strength values were calculated in MPa.

3.6.3 Corrosion resistance:

Corrosion resistance of the 1500°C fired samples were measured against the blast furnace slag, which is having the chemical composition

Table 3.7 Composition of Blast furnace slag

Constituent	**SiO_2**	**CaO**	**Al_2O_3**	**MgO**	**MnO**	**FeO**	**S**
Percentage	31.66	32.25	24.00	5.92	1.25	0.80	0.80

For measuring the corrosion resistance, 50 mm cube shaped samples were prepared with a 15mm hole in the center, which is filled with pellets of 12mm prepared with fine powder of slag, upto the top. After filling the samples were fired at 1500°C with 1hr soaking in a chamber furnace at atmospheric condition.

Sample **Slag** **Cut surface of the corroded Sample**

Figure 3.9 Corrosion resistance

After firing the samples were cut into two halves as shown in fig 3.9 by using a diamond saw cutter which is shown in fig 3.10. The increase in diameter is measured by using vernier caliper.

$$\% \, Corrosion = \frac{D_f - D_i}{D_i} \times 100$$

Here,

D_f = Final diameter after of the hole (after firing)

D_i = Initial diameter of the hole (before firing)

Figure 3.10 Diamond saw cutter

After measuring the corrosion, one half of the sample was taken; it is cut in a way, where slag corroded area and the normal (refractory) area are present in one piece. That is later used for the determination of microstructural analysis.

3.6.4 Phase analysis:

X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material. 1500ºC fired composites were broken into small pieces, then ground to fine powder, characterized for phase analysis by powder x-ray diffraction technique, using Cu Kα radiation through Ni filter, in an x-ray diffractometer (Rigaku, Japan make) shown in fig 3.11. Different phases present and formed were determined by XRD pattern.

Figure 3.11 X-ray Diffractometer

Scan Angle 2θ = 10-60º

Continuous scan speed = 20º per minute

Analysis of obtained diffraction pattern was done by Philips X-pert high score software.

XRD was done on the matrix part only to better identification of reaction product and phases developed in the matrix part, where actually reaction takes place. Aggregates part was avoided to reduce the huge peaks of alumina.

3.6.5 Microstructural analysis:

FESEM (Field Emission Scanning Electron Microscope) uses a focused beam of electrons to generate an image or to analyze the specimen. 1500^{o}C sintered samples was studied in a scanning electron microscope (FEI, US make, model Nova SEM) shown in fig 3.12, for microstructural analysis. For studying the microstructural analysis fracture surface form the sintered samples were taken. It is polished by using three grades of abrasive powders on a glass plate and three grades of diamond pastes on a cloth.

Figure 3.12 Scanning Electron Microscope

EDX analyses were also carried out for the prepared samples. Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. EDX systems are attachments to Electron Microscopy instruments.

Details of the preparation techniques of sol and cement bonded are outlined in flow diagram, given in fig 3.13 & 3.14 respectively.

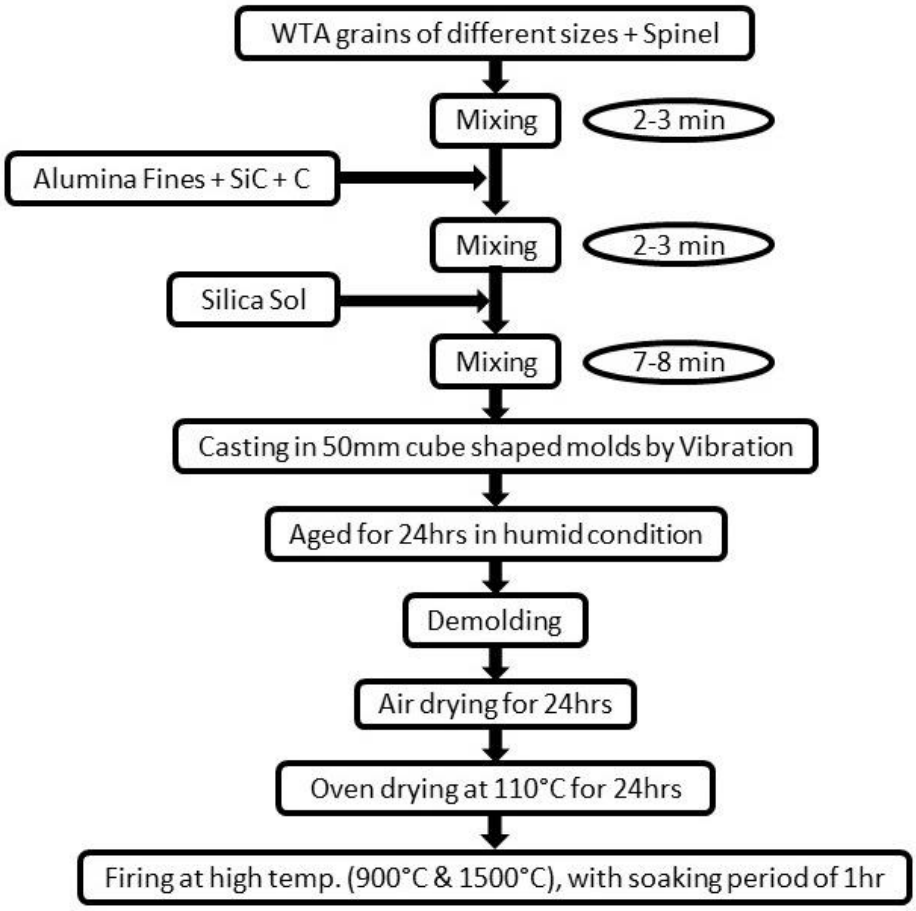

Figure 3.13 Process flow-sheet for sol bonded castables

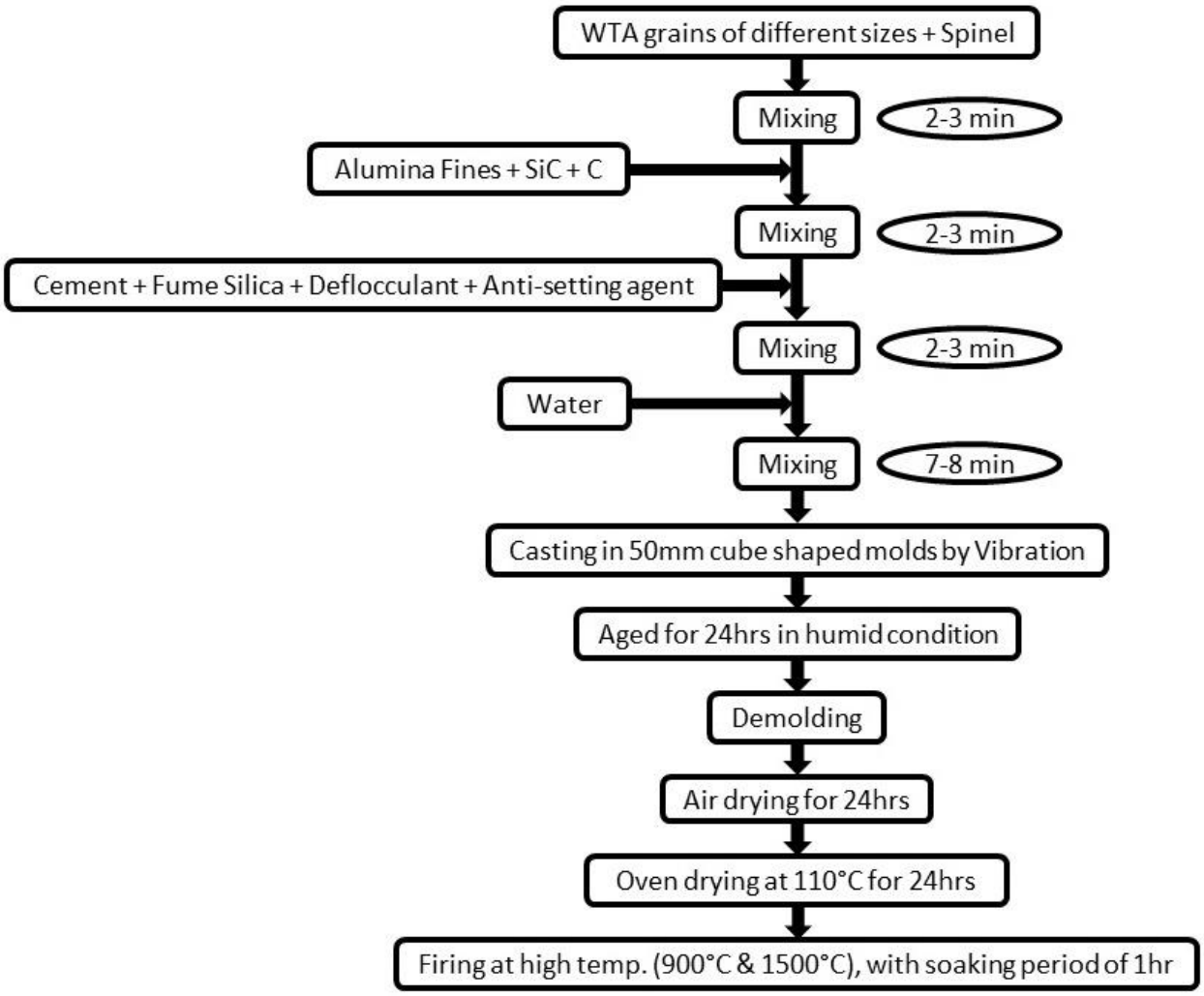

Figure 3.14 Process flow-sheet for cement bonded castables

In the results section, each data represented is an average value of 5 individual samples.

Chapter – 4

Results & Discussions

4. Results and Discussions

Part 1

4.1 Study on the variation in properties with varying amounts of SiC and C without Spinel with q = 0.21

4.1.1 Densification study:

Density values of the samples for both sol and cement bonding systems are decreased with increase in SiC and graphite content and are graphically represented in fig 4.1 & 4.2 respectively. Increase in SiC content reduces the content of alumina. Density of pure alumina has been found to be ~3.97gm/cc and of pure SiC to be ~3.2gm/cc. As the higher density material replaced by the relatively lower density materials, the bulk density of the composition decreases.

In general, there is a marginal fall in density values for all the compositions at intermediate temperatures, due to removal of hydraulic and free moisture and not initiation of sintering. But increase of temperature to 1500^{o}C showed marginal increase in densities which may be due to sintering of the compositions. Higher amount of non-oxides, like SiC and C, reduces the chances of direct bonding / sintering among alumina particles, thereby reducing the sintering and densification [1].

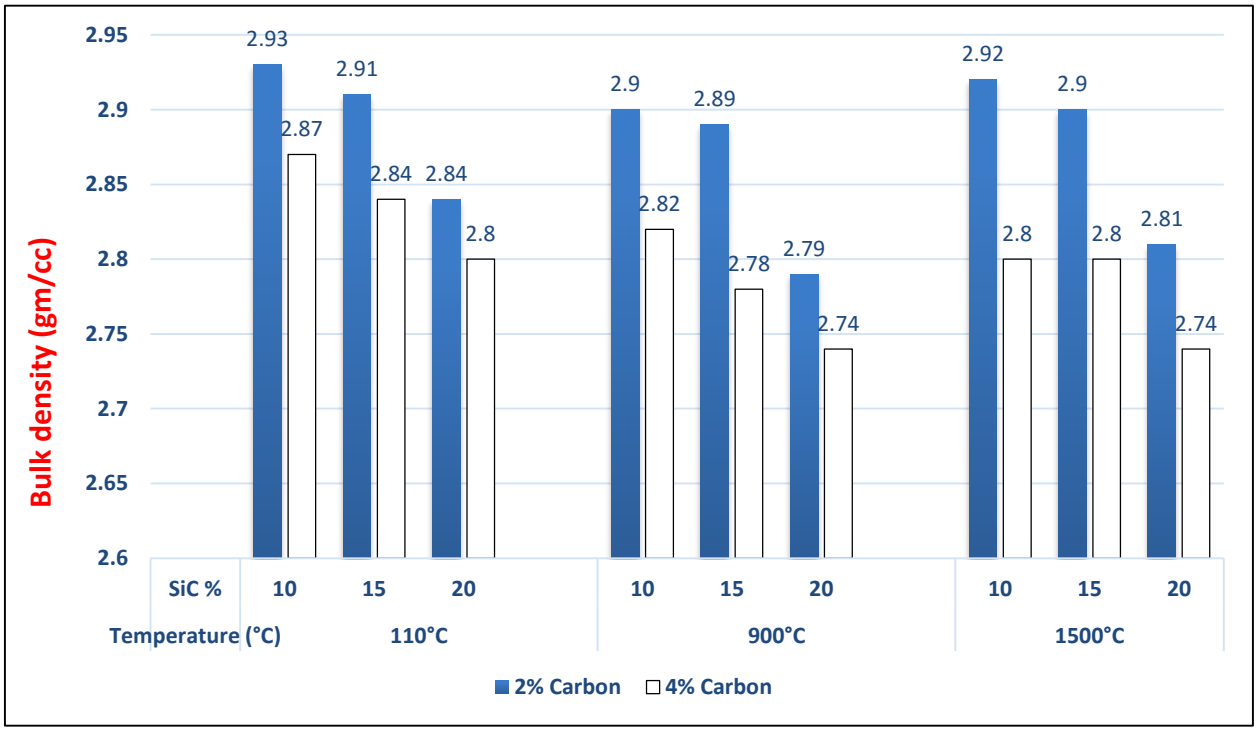

Figure 4.1 Bulk densities of sol bonded compositions

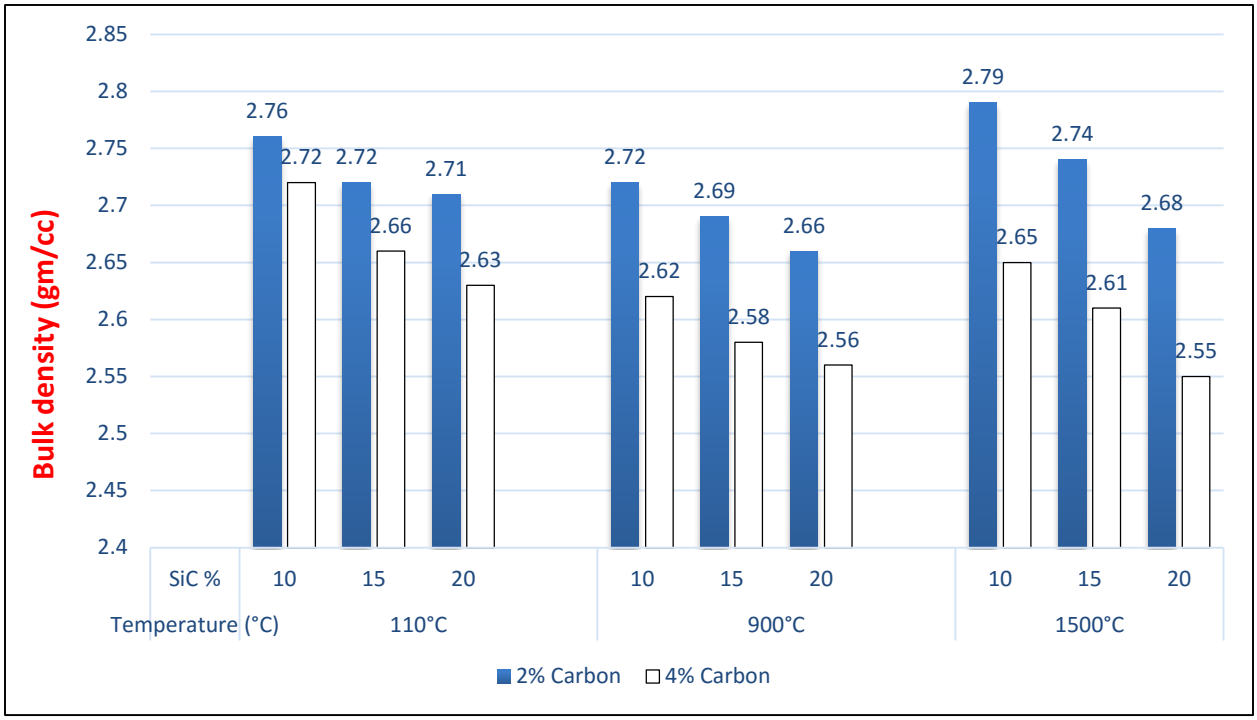

Figure 4.2 Bulk densities of cement bonded compositions

4.1.2 Strength study:

The CCS of the sol and cement bonded compositions are graphically represented in fig 4.3 & 4.4 respectively. Dried strength of cement bonded castables is more compared to sol bonded castables because the cement forms the hydraulic bonding at room temperature which is stronger than coagulation bonding of sol-gel system [2]. Deterioration of strength was observed due to breaking of hydraulic bonding in cement containing composition.

The CCS values for both the bonds are almost similar after sintering because the gel have high surface area and contains finer particles that exhibited better sintering [3]. Strength development is poor especially for cement bonding with higher non oxide content. Also, higher SiC content reduces the chances of direct bonding / sintering among alumina particles, thereby reducing the sintering and densification [4].

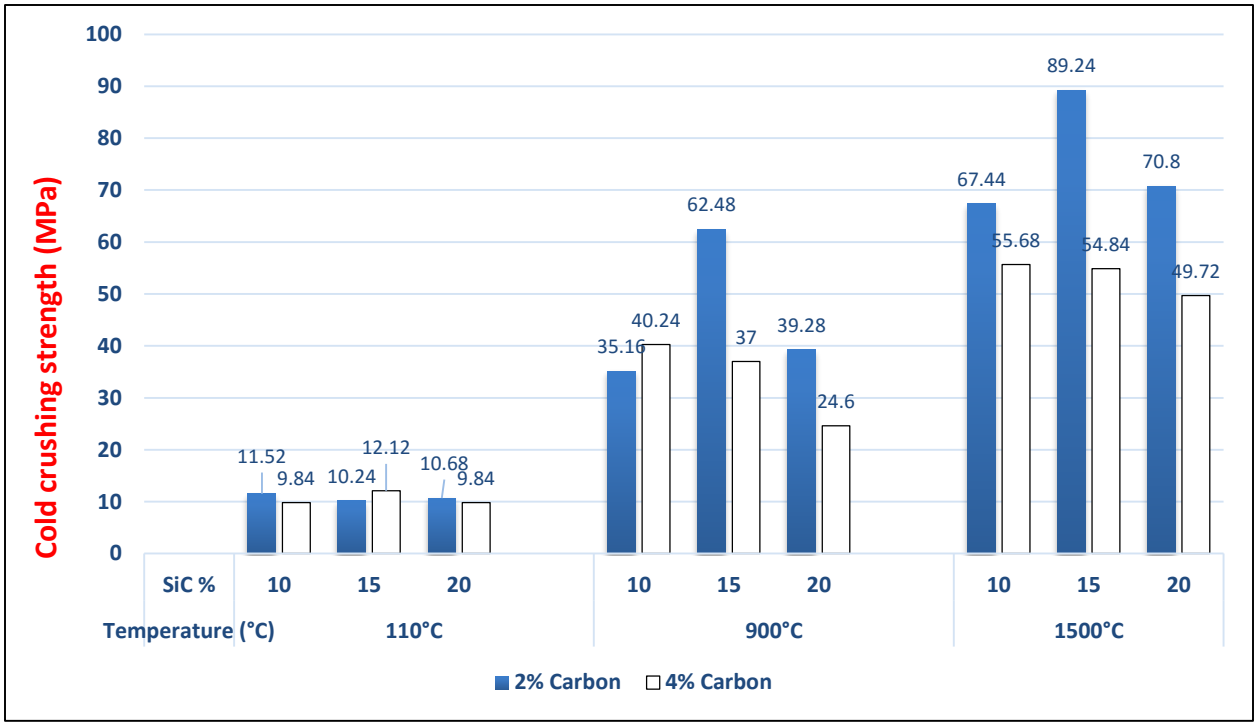

Figure 4.3 Cold crushing strength of sol bonded castables

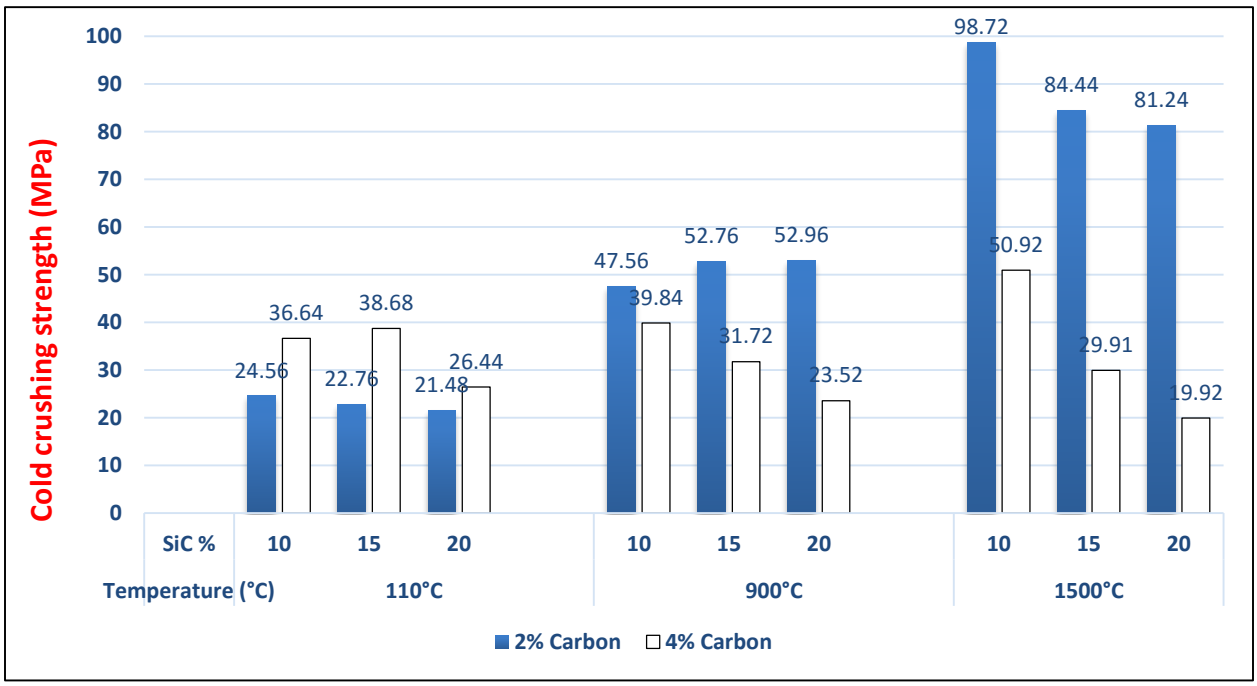

Figure 4.4 Cold crushing strength of cement bonded castables

4.1.3 Phase analysis:

From the phase analysis study, it was found that commonly the major phases present are corundum, SiC, C and mullite in both the bonding systems of trough castables. X-ray diffraction patterns of the 4% graphite containing sol and cement bonded castables, with varying amount of SiC, fired at 1500^{o}C are shown in fig 4.5 & 4.6 respectively.

Mullite is the reaction product formed at high temperature in the matrix part of the castables due to reaction between silica particles from sol and fine alumina particles, alumina fines in sol bonded castables and between fume silica and alumina fines in cement bonded ones. Also presence of mullite phase was found to increase with increasing amount of SiC in both the sol and cement bonded compositions. This may be due to the formation of extra silica on oxidation of SiC during firing which further reacts with fine alumina in the matrix phase forming mullite.

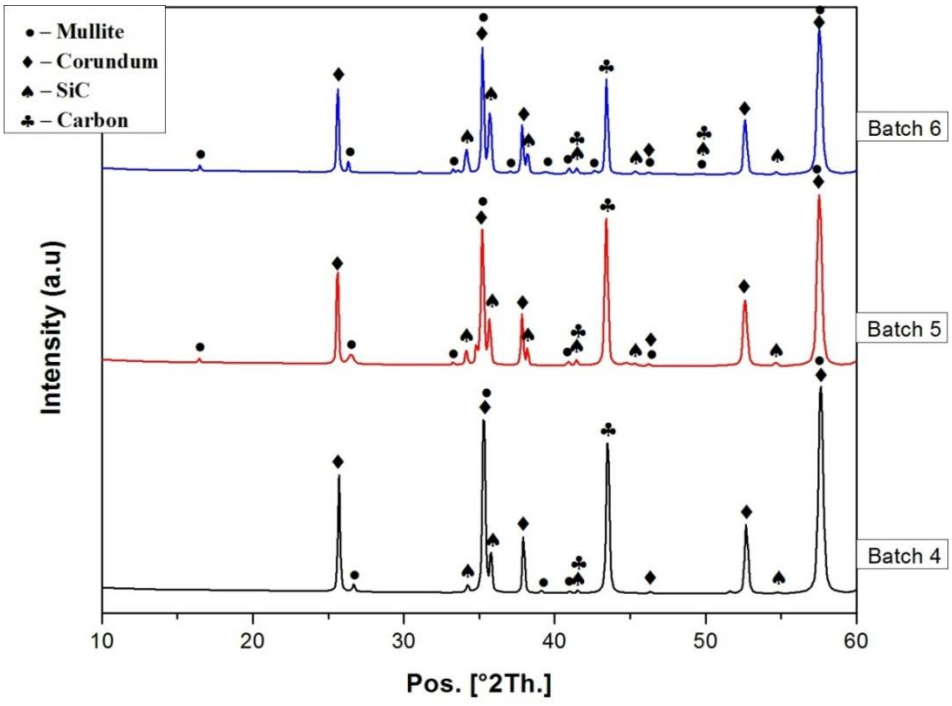

Figure 4.5 XRD of sol bonded castables

Mullite formation is important for strength development in the castable compositions. Again, in the case of cement bonded compositions hibonite and anorthite phases were also found. These lime bearing phases were formed due to reaction between calcium aluminate cement particles with alumina fines and fume silica respectively in the matrix part.

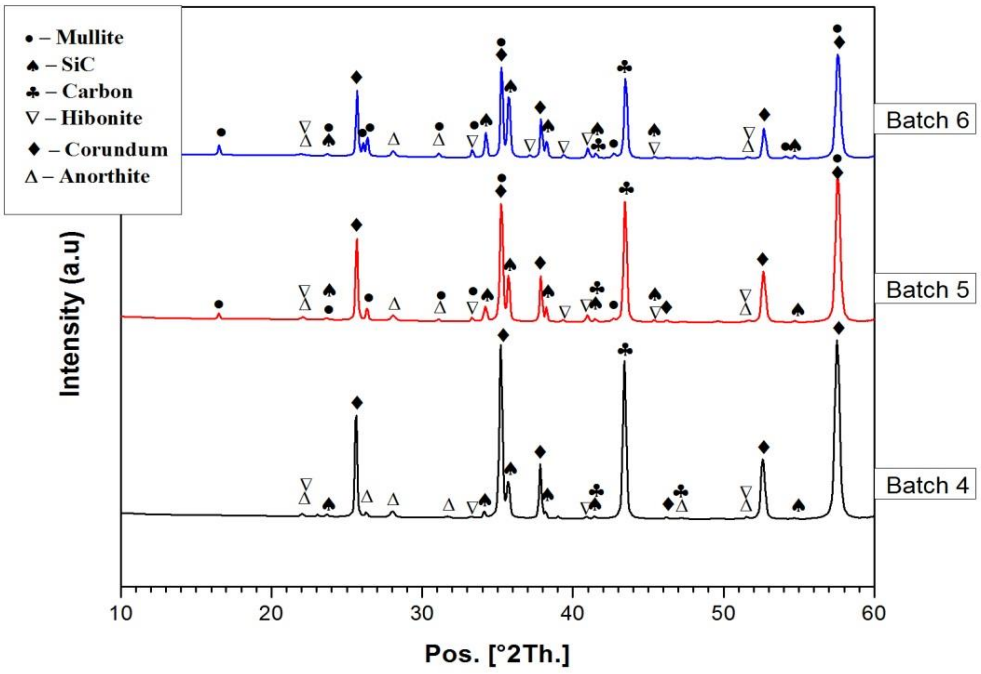

Figure 4.6 XRD of cement bonded castables

4.1.4 Microstructural analysis:

Batch 2, containing 15wt% SiC and 2 wt% graphite shows different microstructural features for cement containing and silica sol containing compositions. Cement containing composition shown in fig 4.7, showed presence of non-uniform sized grains but not in a well compact manner compared to that of well compacted granular structure of different sized grains for sol containing ones showed in fig 4.8. This indicates compaction of cement containing composition resulting in lower density and strength values compared to that of the sol containing compositions. Batch 6,

containing 20wt% SiC and 4 wt% graphite showed granular microstructure but not as very distinct as that of batch 2 for both the cement and sol containing compositions. Cement containing batch 6 showed relatively porous structures with both inter and intra granular pores with grains of less compact and less angular nature shown in fig 4.9. Formation of low-melting compound like anorthite, as found in phase analysis may be responsible for such microstructural development. Batch 6 of sol containing composition shown in fig 4.10, showed well compact more angular grains, indicating higher density and strength characteristics.

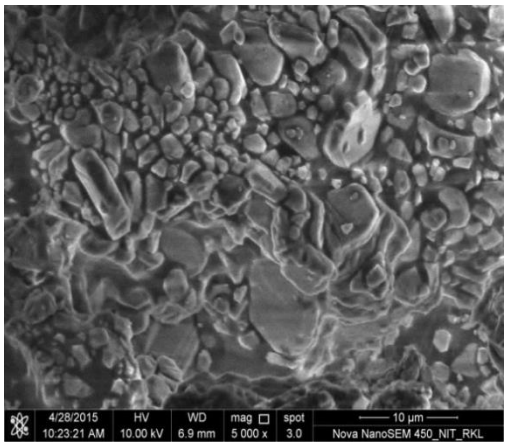

Figure 4.7 Batch 2 cement bonding

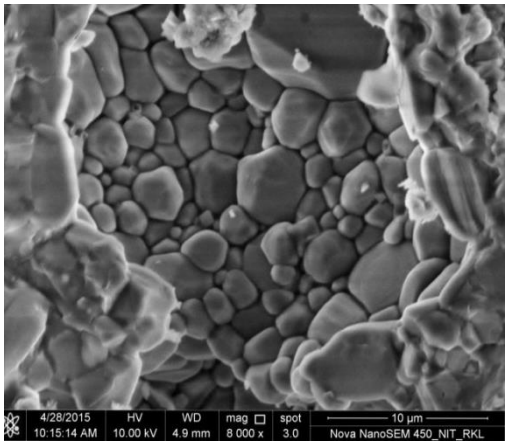

Figure 4.8 Batch 2 sol bonding

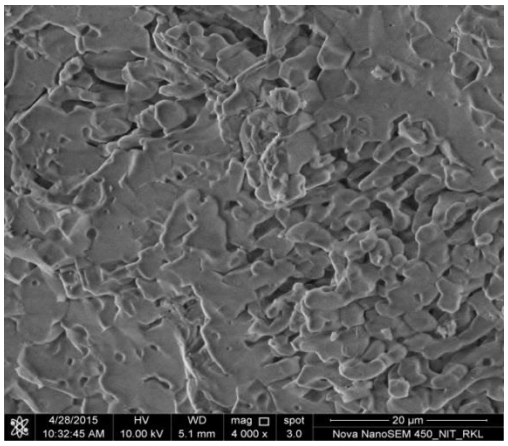

Figure 4.9 Batch 6 cement bonding

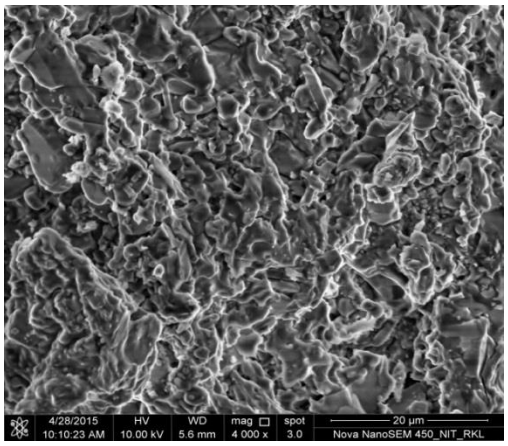

Figure 4.10 Batch 6 sol bonding

Conclusion of 4.1 in Part-1:

- Among the q = 0.21 compositions, 15% SiC containing batches showing better results, so the further q=0.29 study is carried out with optimized 15% SiC containing batches.

Part 1

4.2 Study on the variation in properties with varying amounts of C with 15% SiC without Spinel with q = 0.29

4.2.1 Densification study:

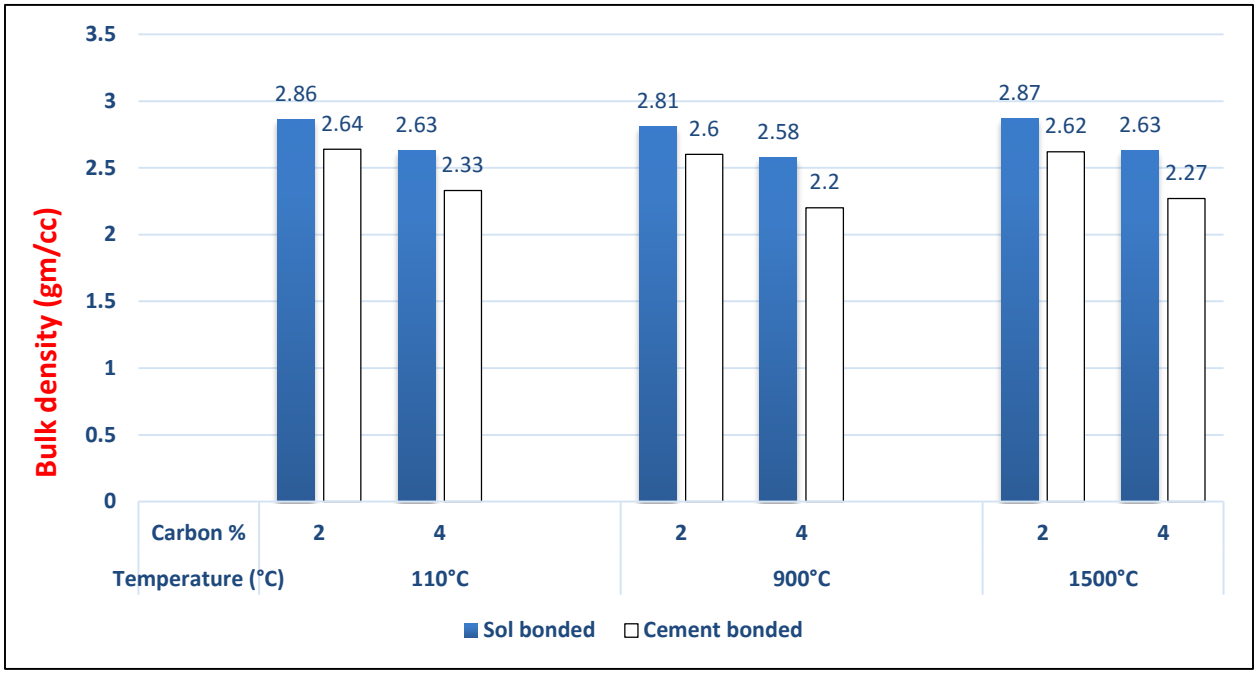

Figure 4.11 Bulk densities of 15% SiC containing both sol & cement bonded compositions

Density values of the both sol and cement bonding systems have decreased with the increase in graphite content are graphically represented in fig 4.11. As the higher density material is replaced by lower density material, the bulk density values have decreased.

It is quite evident from the figure that there is a marginal fall in density values at intermediate temperatures, due to removal of hydraulic and free moisture and not initiation of sintering. Later the bulk density values increased when the temperature is increased to 1500^{o}C, may be due to sintering of the compositions.

4.2.2 Strength study:

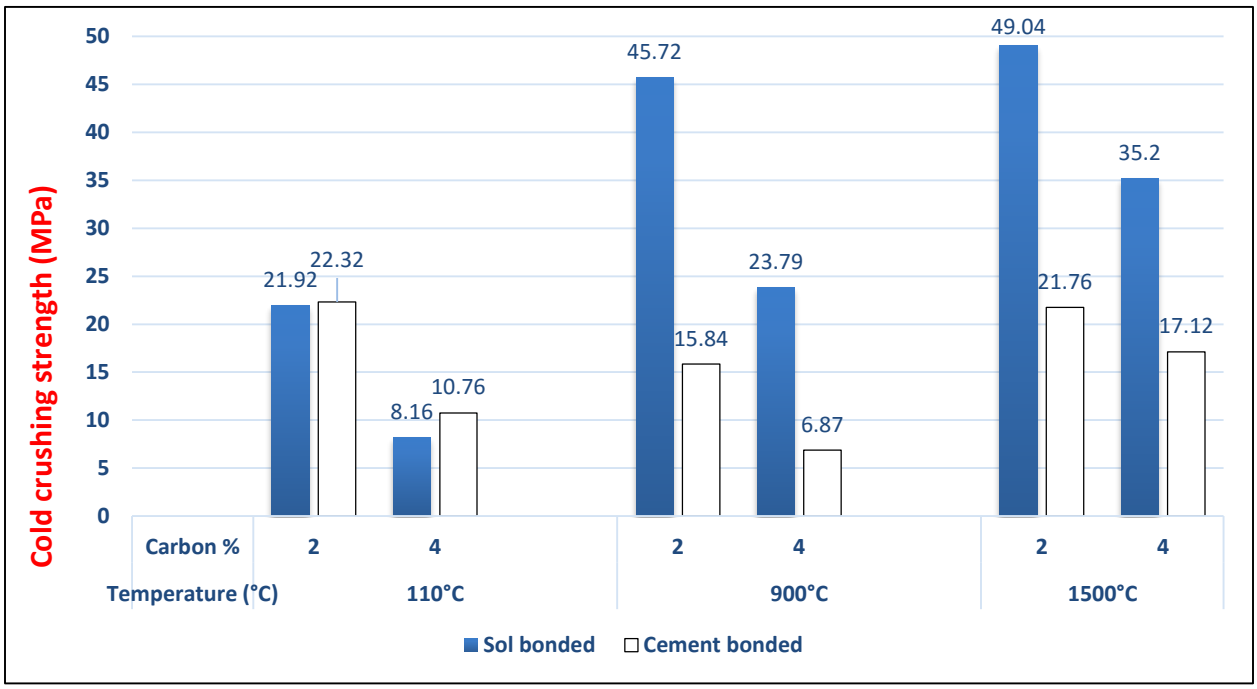

Figure 4.12 Cold crushing strength of 15% SiC containing both sol & cement bonded compositions

The CCS of both sol and cement bonded compositions are graphically represented in fig 4.12. Cement bonded compositions have shown better strength than the sol bonded ones at the dried condition. Cement forms hydraulic bonding at room temperature which is stronger than the coagulation bonding of sol.

Higher amount of fine graphite particles, distributed well in the matrix might have restricted the bonding and strength development. This effect is less prominent for sol containing compositions and may be due to better coating of sol particles over non-oxide components and resulting in better sintering and strength development [1]. The strength values are low for the cement bonded compositions compared to sol bonded compositions at higher temperatures.

4.2.3 Corrosion resistance:

Table 4.1 Detail of the % Corrosion of q = 0.29 Compositions

Batch	Bond	Corrosion %
2% C, 15% SiC	Sol	7.82
2% C, 15% SiC	Cement	15.44
4% C, 15% SiC	Sol	6.95
4% C, 15% SiC	Cement	8.77

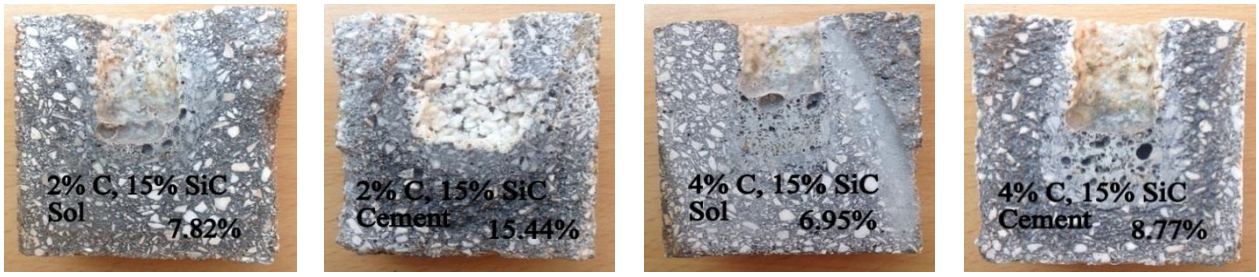

Figure 4.13 Cut surfaces of the corroded samples

The corrosion rate decreases with increase in amount of carbon, because of its non-wetting nature it can avoid adhesion of slag to the castable [5].

Sol bonded castables have shown better corrosion resistance than the cement containing ones. The reason for this may be presence of lime in the cement, which forms low melting phases reacting with the basic components like SiO_2 or Al_2O_3 from the slag [6, 7]. The slag penetration is observed in the case of both cement and sol bonding systems. The increase in q value results decrease in the amount of fines content in the composition resulting in generation of porosity within the system. This might be the reason behind this.

Conclusion of Part-1:

- Among the q = 0.21 compositions, 15% SiC containing one's showing better properties, so the q = 0.29 study is carried out with optimized 15% SiC containing batches.
- The strength values are less in the case of 0.29 compared to 0.21.
- From the comparison q = 0.21 compositions are shown better properties than q = 0.29. So q=0.21 is selected for the addition of spinel.

Part 2

4.3 Study on the variation in properties with varying amounts of C and Spinel with 15% SiC with q = 0.21

4.3.1 Densification study:

Density values of the samples for both sol and cement bonding systems are decreased with the increase in spinel and graphite content are graphically represented in fig 4.14 & 4.15 respectively. Increase in spinel content reduces the content of alumina. Density of pure alumina have been found to be ~3.97gm/cc and of pure spinel to be ~3.58gm/cc.

As the higher density material replaced by the relatively lower density materials, the bulk density of the composition decreases.

At intermediate temperature for all the compositions due the de-hydroxylation of bonds, marginal fall in density occurs. But increase of temperature to 1500^{o}C showed marginal increase in densities, which might be due to sintering of the compositions.

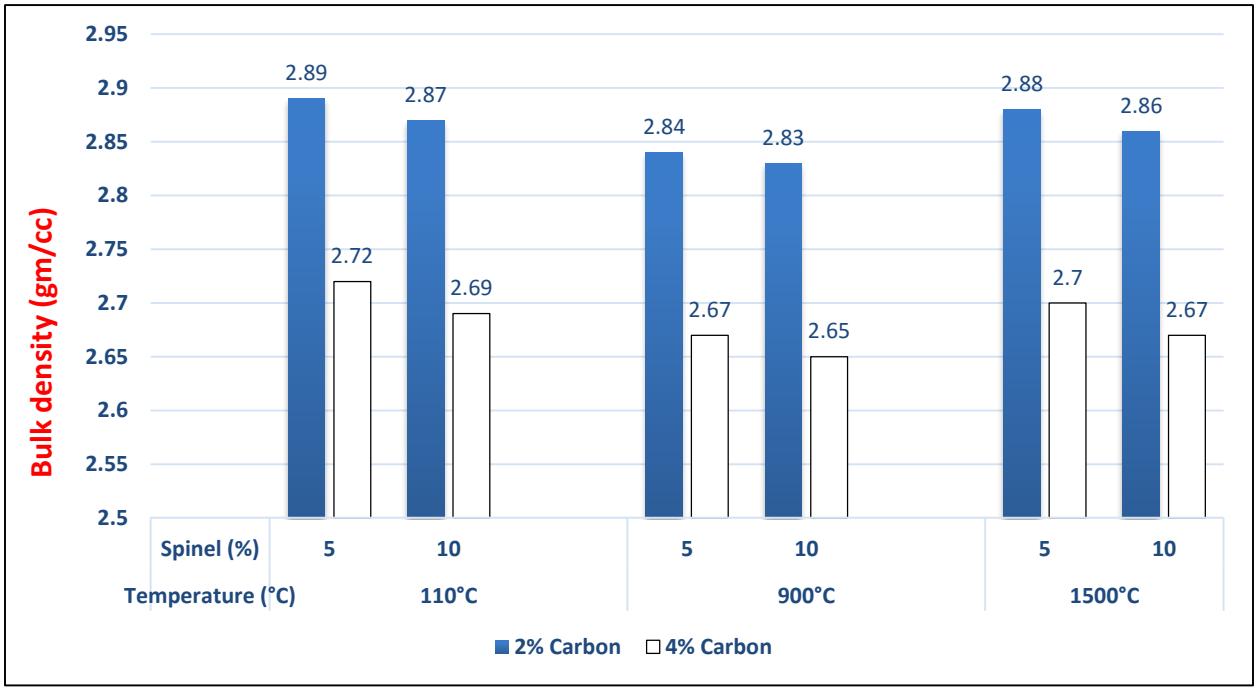

Figure 4.14 Bulk densities of 15% SiC containing sol bonded compositions

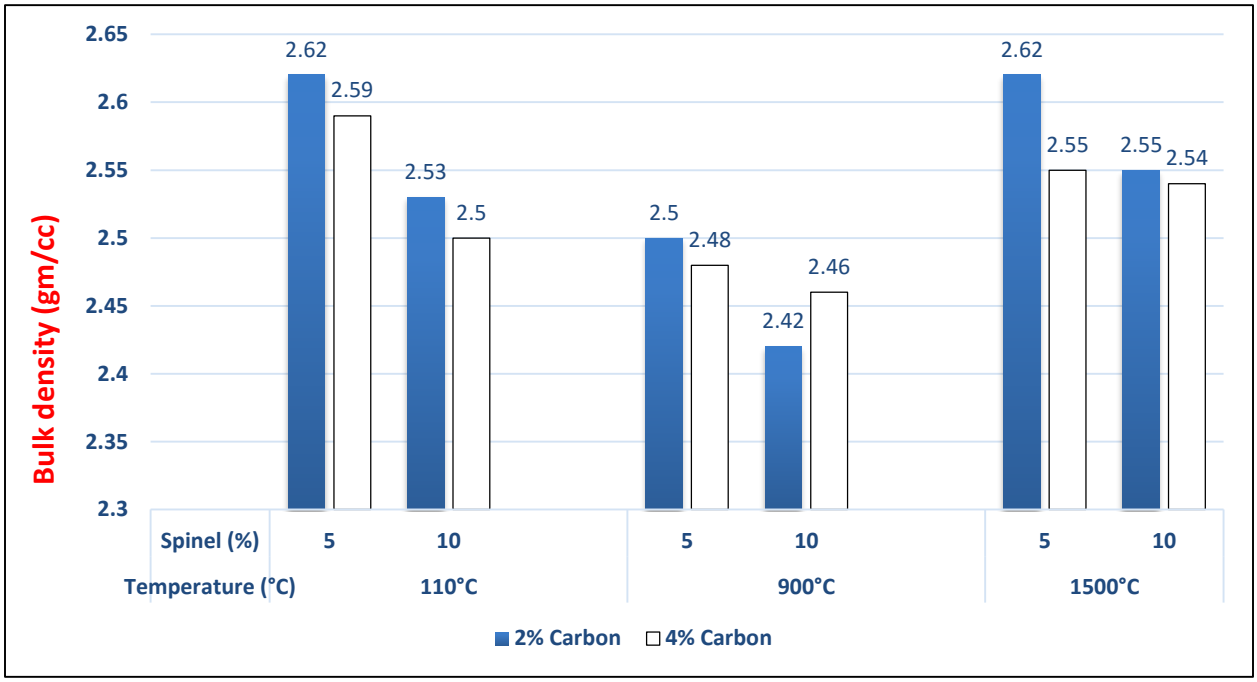

Figure 4.15 Bulk densities of 15% SiC containing cement bonded compositions

4.3.2 Strength study:

The CCS of both sol and cement bonded castables are graphically represented in fig 4.16 & 4.17 respectively. Dried strength of cement bonded compositions are more compared to the sol bonded compositions because the cement forms the hydraulic bonding at room temperature which is stronger than coagulation bonding of sol-gel system [2]. Deterioration of strength was observed due to breaking of hydraulic bonding in cement containing composition.

The CCS values for sol bonded castables are more compared to cement bonded castables after sintering because the gel have high surface area and contains finer particles, which exhibited better sintering [3]. Strength development is poor, especially for cement bonding with higher non oxide content. Higher amount of fine graphite particles, distributed well in the matrix might have restricted the bonding and strength development [4].

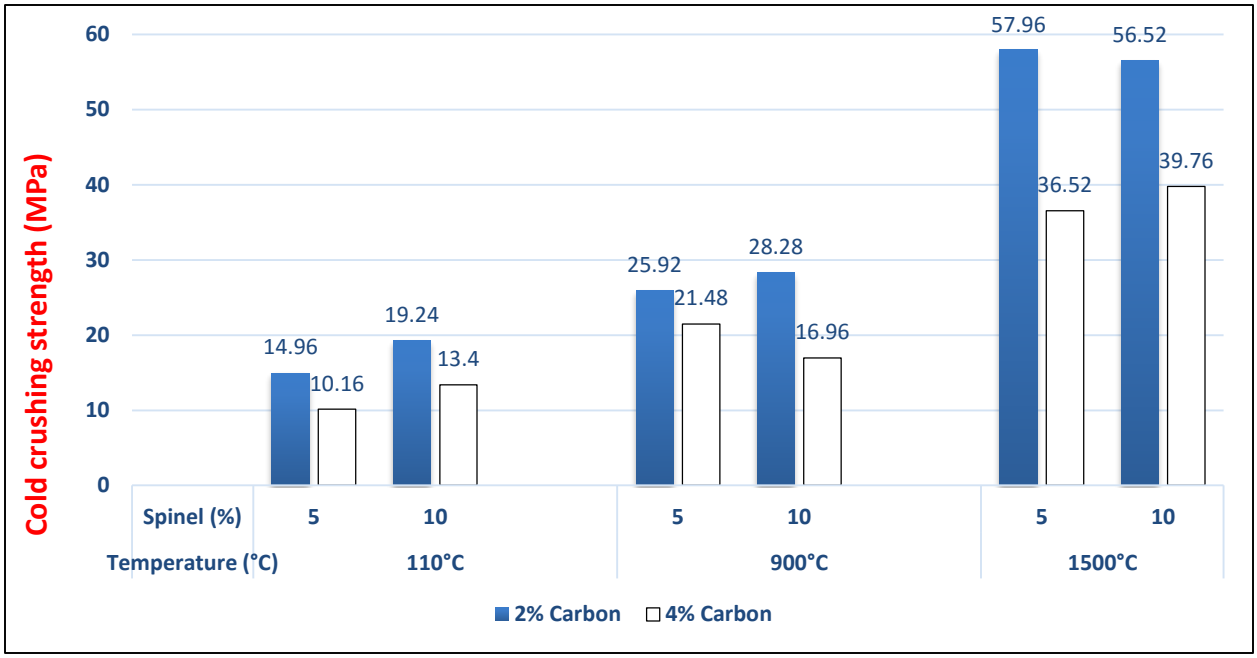

Figure 4.16 Cold crushing strength of 15% SiC containing sol bonded compositions

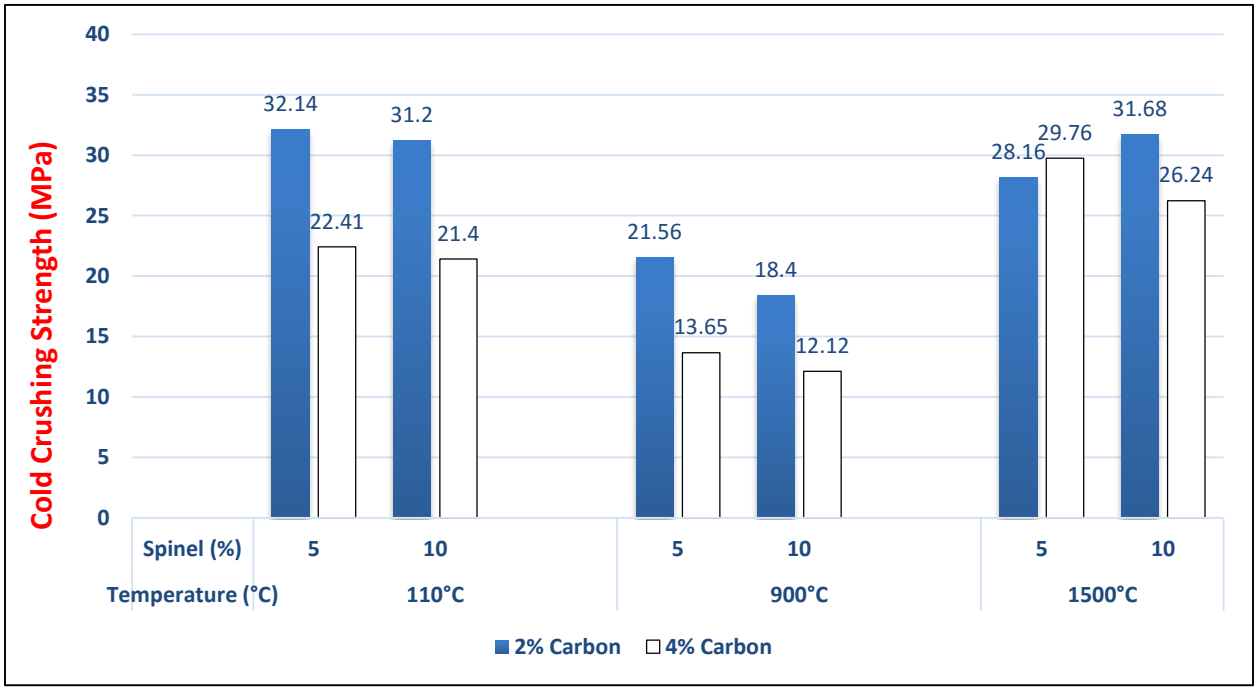

Figure 4.17 Cold crushing strength of 15% SiC containing cement bonded compositions

4.3.3 Phase analysis:

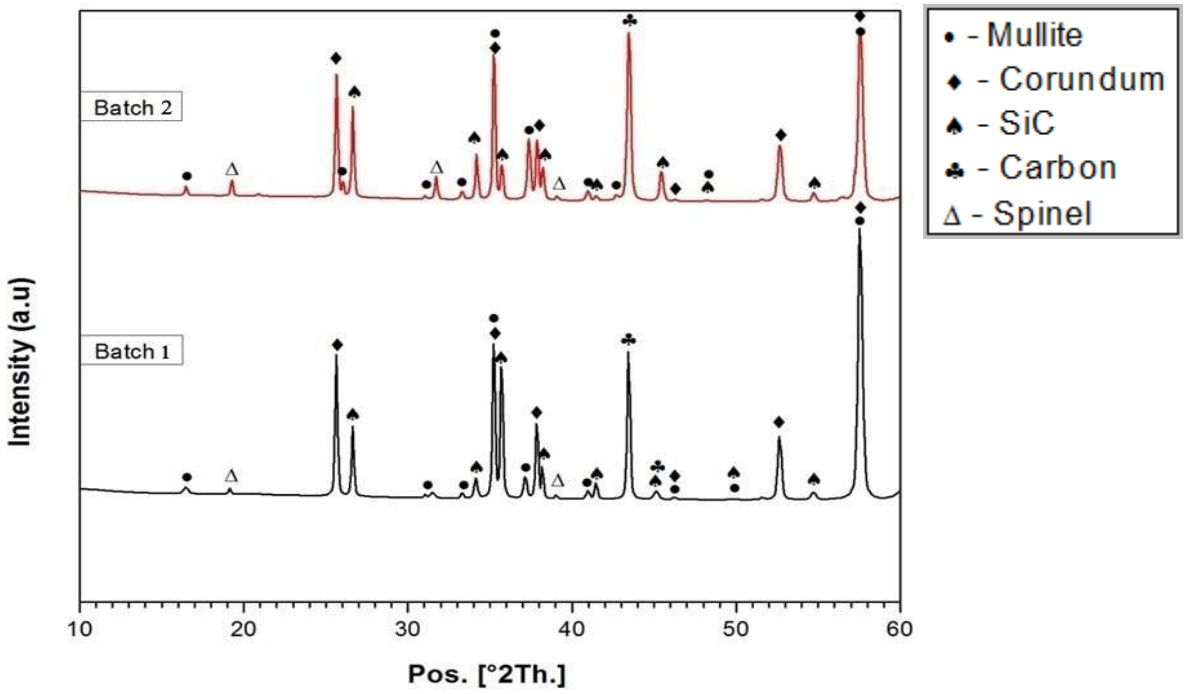

Figure 4.18 XRD of 2% C containing sol bonded castables

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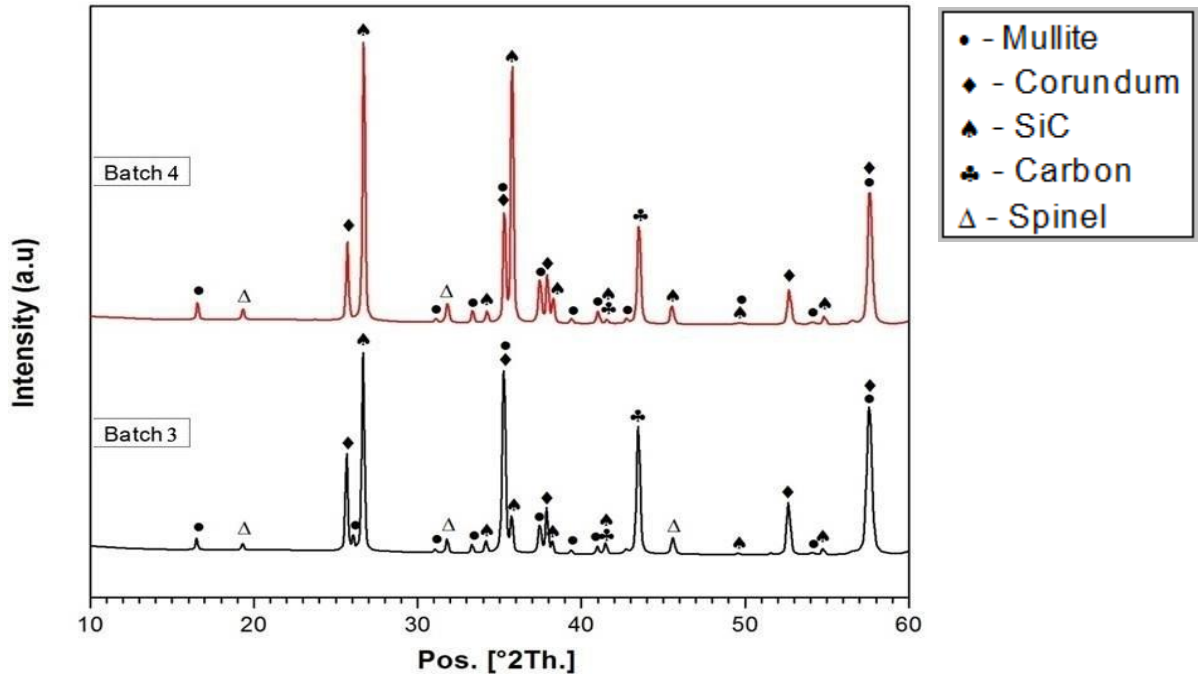

Figure 4.19 XRD of 4% C containing sol bonded castables

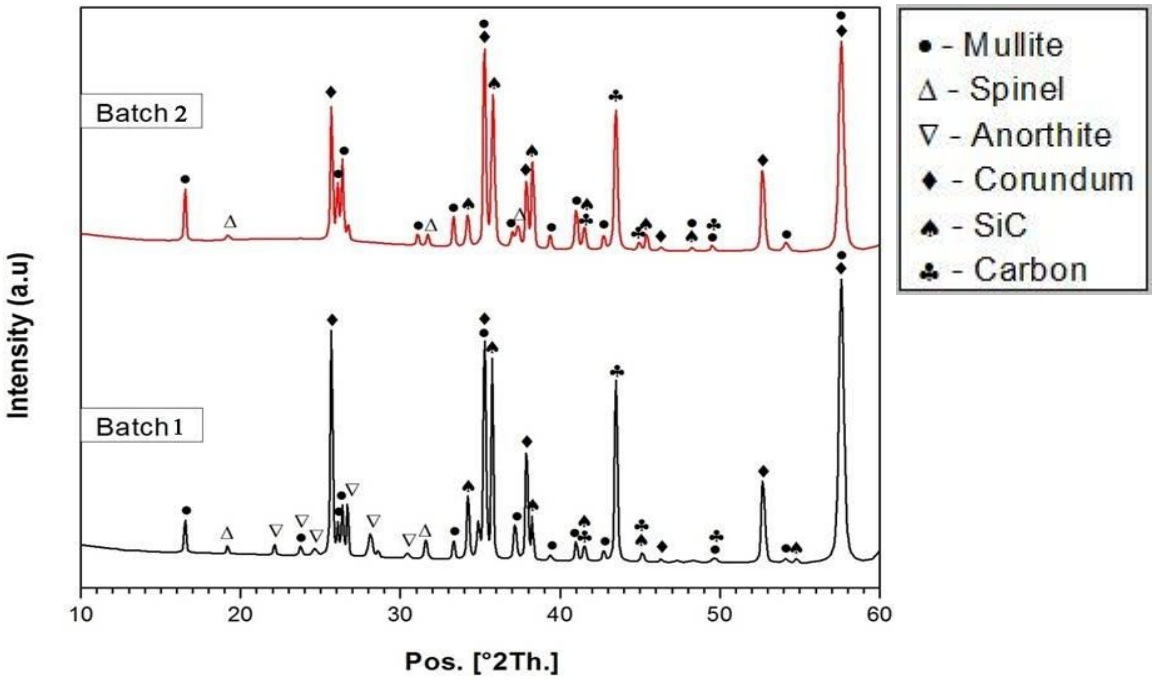

Figure 4.20 XRD of 2% C containing cement bonded castables

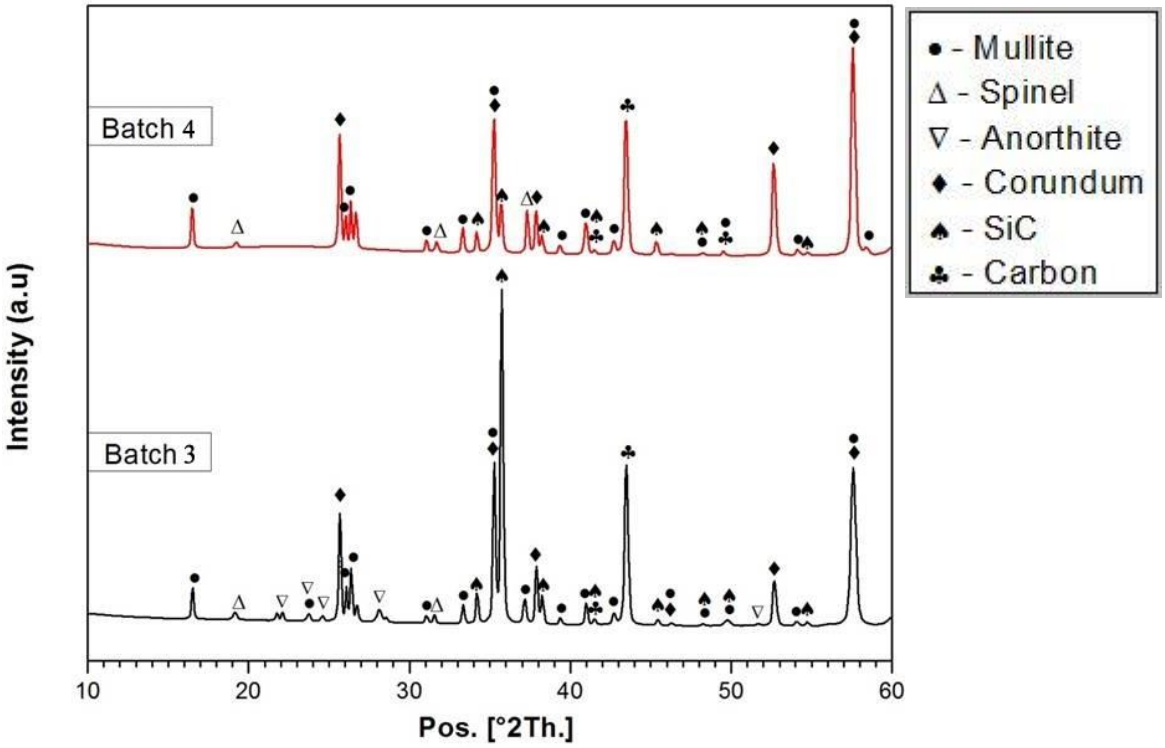

Figure 4.21 XRD of 4% C containing cement bonded castables

From the phase analysis study, it was found that, commonly, the major phases present are corundum, SiC, C, spinel and mullite in both the bonding systems of trough castables. X-ray diffraction patterns of the 2 and 4% graphite containing sol and cement bonded castables, with 5 and 10% Spinel and with same amount of SiC, fired at 1500^{o}C are shown in fig 4.18 - 4.21.

Mullite is the reaction product formed at high temperature in the matrix part of the castables due to reaction between silica particles from sol and fine alumina particles, alumina fines in sol bonded castables and between fume silica and alumina fines in cement bonded ones.

In the case of cement bonded compositions, anorthite phase was found. This lime bearing phase was formed due to reaction between calcium aluminate cement particles with alumina fines and fume silica respectively in the matrix part.

4.3.4 Corrosion resistance:

Table 4.2 Detail of the % Corrosion of q = 0.21 Spinel containing Compositions

Batch	Bond	Corrosion %
2% C, 5% Spinel	Sol	11.61
2% C, 5% Spinel	Cement	12.43
2% C, 10% Spinel	Sol	3.62
2% C, 10% Spinel	Cement	4.52
4% C, 5% Spinel	Sol	5.66
4% C, 5% Spinel	Cement	8.27
4% C, 10% Spinel	Sol	0.95
4% C, 10% Spinel	Cement	1.74

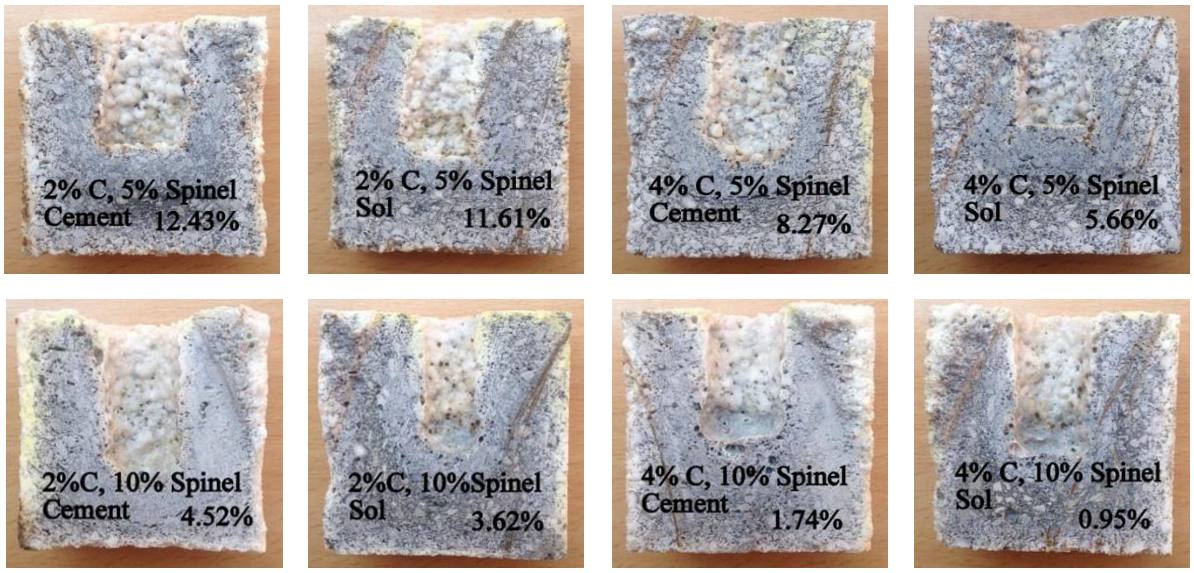

Figure 4.22 Cut surfaces of the corroded samples

The corrosion rate decreases with increase in amount of carbon and spinel in the composition. Because of the non-wetting nature of carbon, it avoids adhesion of slag to the castable [5]. Magnesium aluminate spinel offers high melting point and excellent resistance against chemical attacks [8, 9].

Here also, sol bonded compositions have shown better corrosion resistance compared to the cement bonded compositions.

4.3.5 Microstructural analysis:

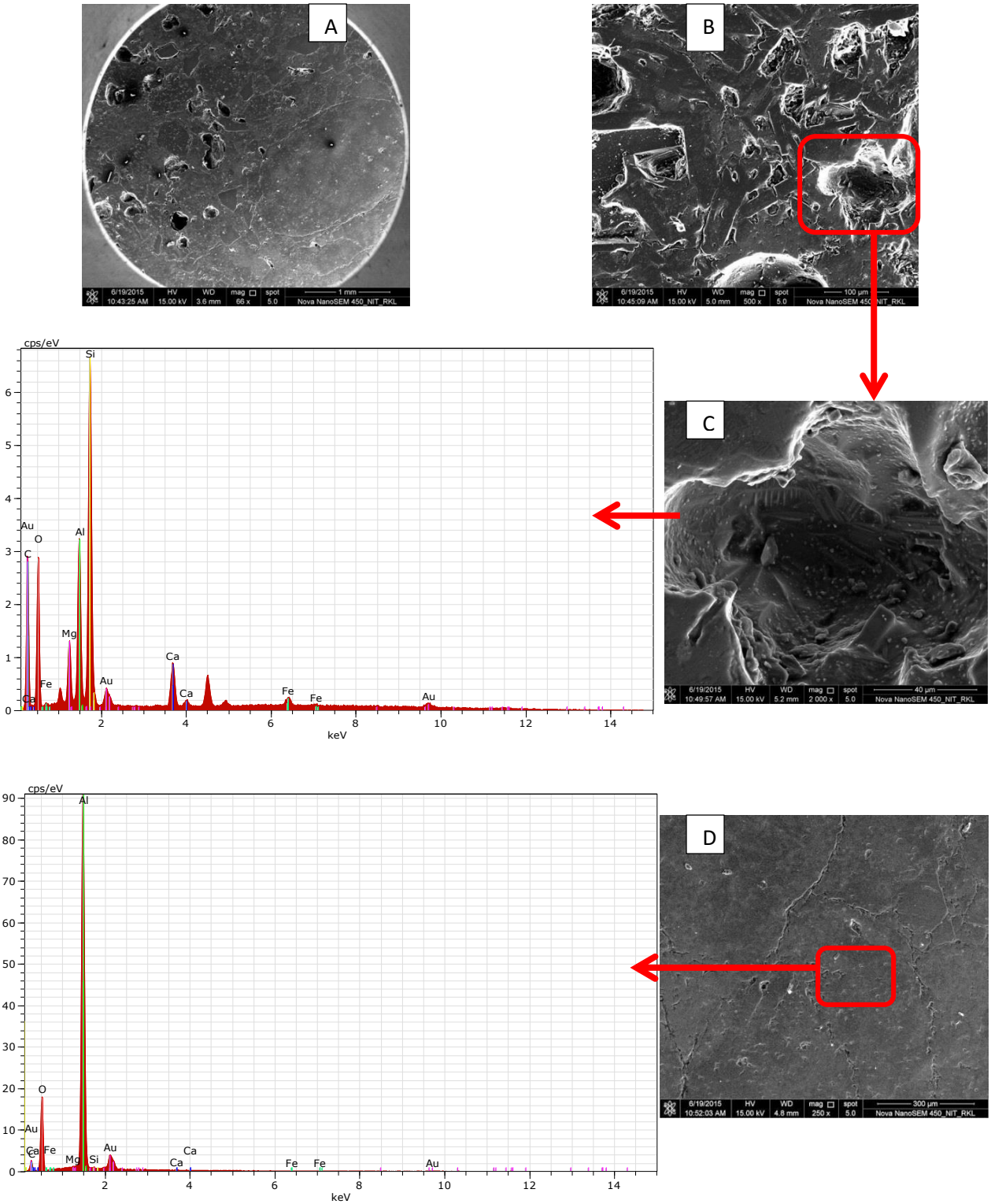

Figure 4.23 Batch 4 sol bonded

The FESEM images of Batch 4 containing 4% Carbon and 10% Spinel sol bonded compositions are given in fig 4.23 with EDS analysis. Fig 4.23 (A) shows well compact dense microstructure of the unreacted refractory (left side of the photomicrograph) but a corroded and porous structure (right side of the photomicrograph) due to the reaction of the sample with the slag. Corroded portion of the fig 4.23 (A) shown in fig 4.23 (B).

Microstructure of one pore from slag corroded area is shown in fig 4.23 (C) with EDS analysis, showing silica, magnesium, calcium and some iron which came from the penetration of slag. Fig 4.23 (D) showing dense, well compacted grains with nearly no porosity was observed. From the EDS analysis aluminum was found to be the only prominent element with oxygen and carbon and nearly no trace of any other impurity element phase.

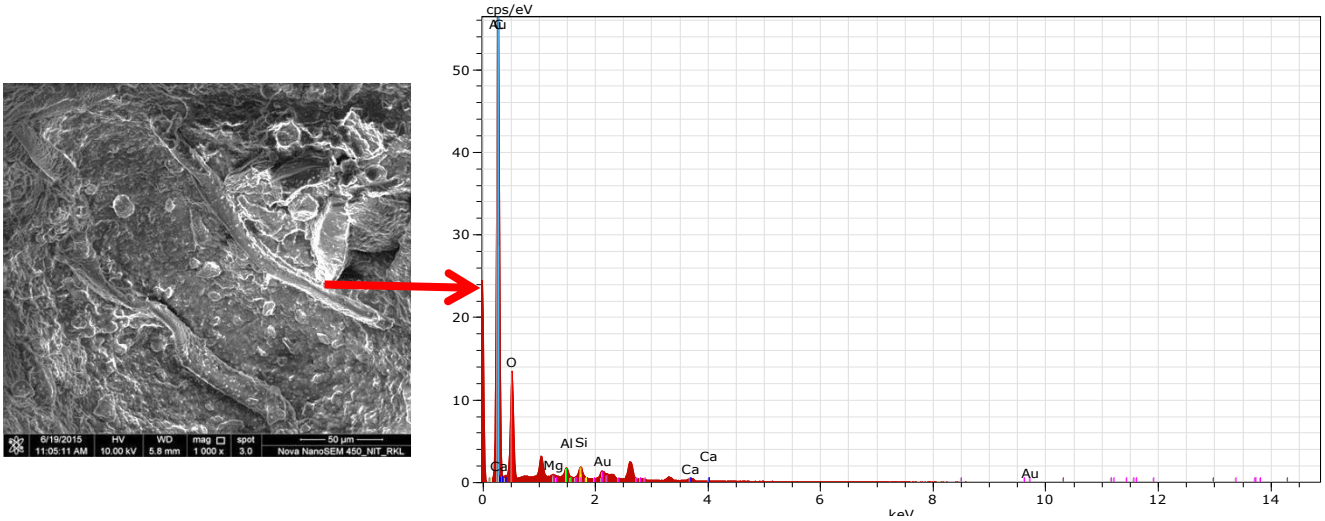

Figure 4.24 Batch 3 sol bonded

Microstructure and EDS analysis of batch 3 containing 4% Carbon and 5% Spinel of sol bonded are shown in fig 4.24. From the EDS analysis, it is conformed that the flake like structure present was graphite. The non- wetting nature of the graphite is visible here, the upper portion of the flake showing more porous structure than the lower portion. This shows that presence of graphite restricts the slag attack and the refractory part remain intact, as observed at the below portion of the graphite flake.

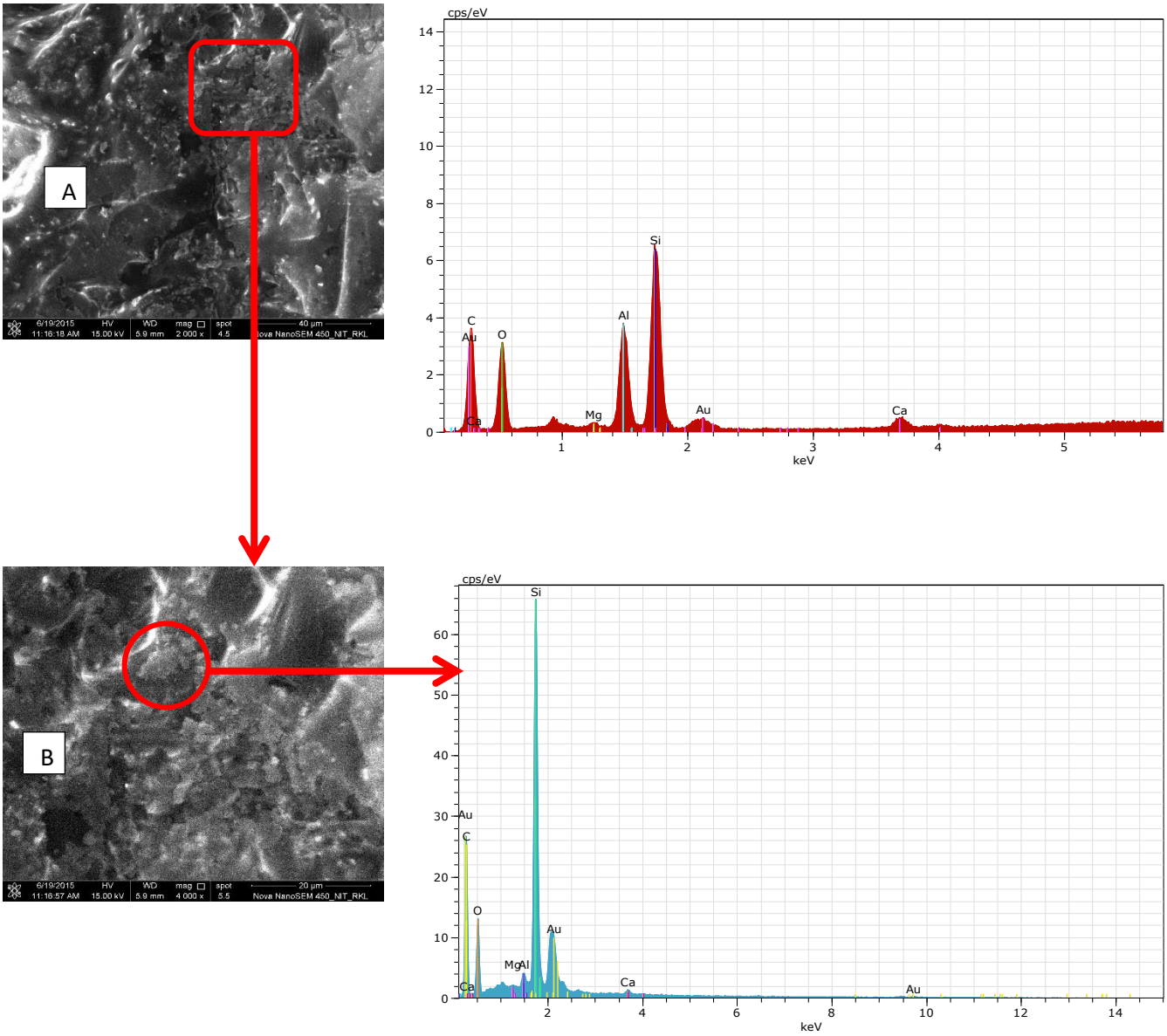

Figure 4.25 Batch 3 cement bonded

Microstructure and EDS analysis of Batch 3 containing 5% spinel and 4% carbon containing cement bonded are shown in fig 4.25. Fig 4.25 (A) showing the microstructure of corroded portion with EDS analysis, showing presence of silicon, aluminum, calcium and magnesium with oxygen and carbon. This conforms the phases like Al_2O_3, MgO, CaO, SiO_2, C etc. This also supports the formation of anorthite phase, as already observed in the phase analysis study.

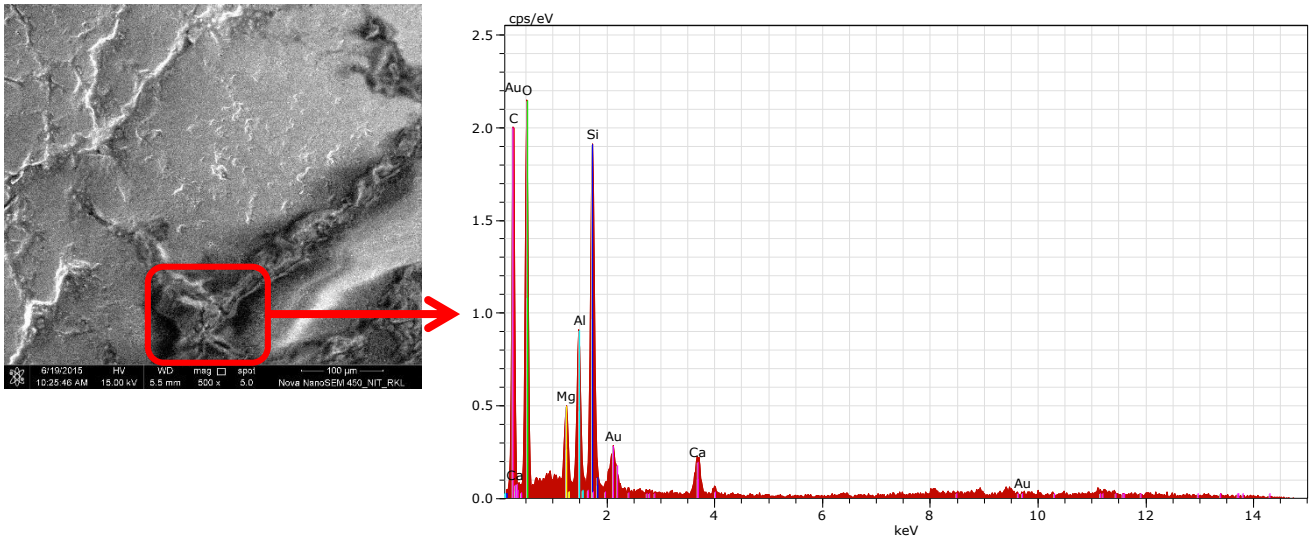

Figure 4.26 Batch 1 sol bonding

Microstructure and EDS analysis of Batch 1 containing 2% carbon and 5% spinel of sol bonded composition are shown in fig 4.26. There is presence of some liquid like structure which is marked on the image. From the EDS analysis it is conformed as silicate phase.

References:

1. Subrata Banerjee, “Monolithic Refractories”, World Scientific Publishing, United States-of America (1998).
2. Z. Li, G. Ye, P.R. China, “Bonding and recent progress of Monolithic Refractories”, Interceram. Vol.41 No.3, (1992) 169-172.
3. T.K.Mukhopadhyay, Ritwik Sarkar, S.K. Das, S. Ghosh and S. Ghatak, “Effect of Synthetic Mullite Aggregate on Clay-Based Sol-Bonded Castable”, Bulletin of the American Ceramic Society (2005) 9101-9104.
4. Wang Cheng, He Zhongyang, Xu Jialiang, “Development and application of castable for BF trough and iron runner”, 2nd International Conference on refractories Jamshedpur (2010) 90-96, Jamshedpur, India.
5. D. N. Borzov, “Development of low cement castables of the Al_2O_3 – SiC – C system”, Refractories and Industrial Ceramics, 43 [3 – 4] (2002) 141-44.
6. Ritwik Sarkar, Somnath Mukherjee and Arup Ghosh, “Gel-Bonded Alumina–Silicon Carbide–Carbon-Based Blast-Furnace Trough Castable”, Bulletin of the American Ceramic Society, (2006) 9101-9105.
7. Sasan Otroj, Mohammad Ali Bahrevar, Fatollah Mostarzadeh, Mohammad Reza Nilforoshan, “The effect of deflocculants on the self-flow characteristics of ultra-low-cement castables in Al_2O_3–SiC–C system”, Ceramics International 31 (2005) 647–653.
8. R. Sarkar, “Refractory Applications of Magnesium Aluminate Spinel”, Refractories Manual (2010) 11-15.

9. Yung-Chao Ko, **“**Influence of the Characteristics of Spinels on the Slag Resistance of Al_2O_3–MgO and Al_2O_3–Spinel Castables”, Journal of the American Ceramic Society, 83 [9] (2000) 2333–35.

Chapter – 5

Summary

5. Summary of the Results:

- Al_2O_3-SiC-C based refractory castables with alumina cement and silica sol bonding were developed with a q values 0.21 and 0.29 as per Dinger & Funk.
- The Bulk density of the compositions decreases with increase in amount of C, SiC and Spinel content.
- The CCS values for the cement bonded castables in the dried state are higher compared to the sol bonded castables because of the stronger hydraulic bonds.
- Silica sol containing compositions showed no degradation in strength at intermediate temperatures; also formation of mullite provides further bonding and increased strength at higher temperatures.
- Phase analysis confirms the formation of mullite phase. Also lime bearing hibonite and anorthite phases were found in cement containing compositions.
- Increase in spinel content in the castable increases the corrosion resistance.
- In slag, the main penetrating and corroding components are SiO_2, CaO and Fe oxides.
- Graphite flake was found to prevent slag penetration.
- Sol containing castables showed better corrosion resistance compared to the cement bonded castables.
- 2% C, 15% SiC and 10% Spinel containing sol bonded composition was the optimum batch on the basis of properties obtained.

RÉSUMÉ

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Career Objective:

I aim to obtain the position of an Engineer in a respectable firm where I can fully utilize my talents, knowledge and inter-personal skills for the benefit of myself as well as the firm.

Educational Credentials:

Course	Discipline	School/College	Board/ University	Year of Passing	%
M.Tech (R) (Present)	Ceramic Engineering (Refractories)	NIT Rourkela	NIT	2015	87.1 (till date)
B.Tech	Ceramic Technology	Andhra University College of Engineering	Andhra University	2012	78.1
Intermediate	M.P.C	Narayana Jr College	Board of Intermediate Education.	2008	89.8
S. S. C	S.S.C	RCM High School	Board of Secondary Education	2006	84.6

Publications:

1. **A comparative study on bonding systems in alumina-silicon carbide-carbon based trough castable,** Venkatesh Pilli and Ritwik Sarkar, accepted in Journal of iron making and steel making.
2. **Effect of spinel content on the properties of Al_2O_3-SiC-C based trough castable,** Venkatesh Pilli and Ritwik Sarkar, Ceramics International **42** (2016) pp.2969-2982.

Conferences / Presentations:

1. Presented a Paper on "**Al_2O_3-SiC-C based blast furnace trough castable: comparison between cement and sol bonding**" in International conference on Refractories held at Jamshedpur in 2015.
2. Presented a poster on "**Ceramics in Electronics"** in Concert-11 - A National level symposium conducted by Anna University Chennai in 2011.

Industrial Training:

One month in-plant training on "Manufacturing process of ceramic tiles" at Regency Ceramics Limited, Yanam, Andhra Pradesh, April 2011.

Industrial visits:

- Vizag steel plant; Swetha refractories; WS Insulators

Academic Projects:
Bachelor's Degree:

Title: Manufacturing of different types of glass and their applications
Institution: Andhra University, Visakhapatnam

Master's Degree:

Title: Al_2O_3-SiC-C based blast furnace trough castable: comparison between cement and sol bonding.
Field: Unshaped Refractories
Institution: NIT Rourkela

Technical Expertise:

- X'pert high score analysis and Origin plot.
- Knowledge in windows operating system – 7, 8.
- Microsoft Office.
- Certification in "Diploma in computer applications".
- Certification in "C" language.

Extra-Curricular Activities:

- Participated as a volunteer in University level Academic exhibition conducted by Andhra University.
- Received Nehru Pratibha award in a Quiz competition conducted by NSUI.

Languages known : Telugu, English and Hindi
Hobbies : Playing Badminton, Cricket and Carroms

Profile:

Name	:	Venkatesh Pilli
Date of Birth	:	04-Aug-1991
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Declaration:
I hereby declare that the above-mentioned information is correct up to my knowledge and I bear the responsibility for the correctness of the above-mentioned particulars.

Place: Rourkela **Venkatesh Pilli**
Date: 14-12-2015